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THE DISTRIBUTION OF FLUORIDE IN SOUTH AFRICAN GROUNDWATER AND THE IMPACT THEREOF ON DENTAL HEALTH

BY

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THE NEED FOR SAFE AND ADEQUATE WATER

" So Moses brought Israel from the Red Sea and they went out into the wilderness of Shur, and they went three days in the wilderness and found no water. And when they came to Marah, they could not drink of the waters of Marah, for they were bitter: therefore the name of it was called Marah. And the people murmured against Moses, saying, " What shall we drink? And he cried unto the Lord, and the Lord showed him a tree, which when he had cast into the waters, the waters were made sweet"

<u>Exodus 5: 22 - 26</u>

DEDICATION

This dissertation is dedicated to all those who have fought to liberate the oppressed, who have managed to eliminate the barriers that limit the normal social associations of all human kind and who have realized the need of encouraging women to participate in collaborative research and a recognition of their cognitive skills and payment of the human debt

ABSTRACT

The most appropriate and widely used source of drinking water for the rural populations of South Africa is groundwater. Pilot studies and surveys conducted by the Department of Water Affairs and Forestry (DWAF) indicated that there are a number of boreholes across the country that contain apart from fluoride, levels of nitrate, some heavy metals, total dissolved solids, sulphates and faecal coliform (in isolated regions) that could pose a health risk if the water is used for drinking purposes. Very few boreholes have been tested for heavy metals or toxic organic substances. However considering the levels of fluoride, in general, groundwater is of acceptable quality except for some provinces in which elevated levels of natural groundwater fluoride occurs. Very high levels of fluoride, >4 mg/l occur in some groundwater sources in all nine provinces of South Africa, especially in the Limpopo, North-West, Eastern Cape, Northern Cape, Western Cape and KwaZulu Natal provinces. A superficial inspection reveals that most of the local people in those areas suffer from dental fluorosis at varying degrees. The main aim of this study is to determine the distribution of the fluoride ion concentration levels in South African groundwater and the impacts thereof on dental health. The available data is used to assess the distribution of the various fluoride ion concentration levels in some national groundwater sources. Areas of particularly high or low fluoride levels are identified. Results from an epidemiological survey carried out by the National Department of Health (NDOH) are used concurrently with the fluoride data to determine the percentage morbidity of dental fluorosis in each area. The results are compared in order to determine if any relationship exists between the occurrence of fluoride in drinking water and the incidences of dental fluorosis. Vegter's lithostratigraphy and the simplified geology of South Africa are used to interpret the results and assess the role of surface geology in the release and distribution of fluorides in groundwater. The role of other factors such as climate and the interactions of the fluoride ion and other water quality parameters in aqueous media are also assessed.

Keywords: groundwater, fluorides, dental fluorosis, geochemistry, morbidity of dental fluorosis, climate, water quality.

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SYMBOLS AND ABBREVIATIONS

DWAF:	Department of Water Affairs and Forestry
NDOH:	National Department of Health
SAWB:	South African Weather Bureau
SABS:	South African Bureau of Standards
ANON.	Anonymous
WQM:	Water Quality Monitoring
TWQR:	Target Water Quality Range
CEV:	Chronic Effect Value
AEV:	Acute Effect Value
WMS:	Water Management System
NGDB:	National Groundwater Database
USNRC:	United States National Research Council
WRC:	Water Research Commission
WHO:	World Health Organisation
F	Fluorine
F^-	Fluoride ion
SI	Saturation Index
SP	Saturation Percentage
USPHS	United States Public Health Society
AWWA	American Water Works Association
OFS	Orange Free State
RSA:	Republic of South Africa
EC	Electrical Conductivity
C_{opt}	Optimum Concentration
°C	Degrees Celsius
TAL	Total Alkalinity
GIS	Geographic Information Systems
WMA	Water Management Area
SSA	Statistics South Africa
CDTA:	Cyclohexene diamine tetra acetic Acid

TISAB	Total Ionic Strength Adjustment Buffer
SAWQG:	South African Water Quality Guidelines
DOH:	Department of Health
WC	Western Cape
NW	North-West
KZN	KwaZulu Natal
QUALDB	Quality database(National water quality database housed at DWAF)
FS	Free State
K_{sp}	Solubility product constant
$_pK_{25°C}$	Solubility product at 25 °C
kg	Kilogram
g	gram
µg	microgram (0,000 0001g)
mg	milligram (0,001g)
ppm	parts per million or mg/kg solid equivalent to 1mg/l in solution.
T	Temperature in degrees Celsius.
P-Tri	Irrigasie sediments (mudstone/siltstone)
Pe	Ecca shale
Jd:	Dolerite dyke/silt
Vma:	Sandstone

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

The beneficial attributes of fluorides to human health have been known for many years (WHO, 1970). The fluoride ion is a very important dietary substance. When ingested at specific doses, the fluoride ion is beneficial to both bone and dental development in human beings. At correct intake levels it plays a very important role in the formation of teeth (Pontius, 1991). Too low fluoride intake levels during childhood may give rise to the occurrence of preventable dental caries in later years. Dental caries is a disease caused by specific bacteria harbored in dental plaque, fermenting carbohydrates to produce acids that can demineralise tooth enamel (Hammer, 1986). If this demineralization is allowed to continue, the enamel is penetrated permitting bacterial invasion and eventual loss of the tooth by decay in the absence of restorative dental care.

Too high fluoride intake normally gives rise to teeth mottling (dental fluorosis) and related problems. Chronic endemic fluorosis is a condition which is caused by an excess of fluorides in drinking water and which affects the calcification of the teeth, resulting in what is commonly known as dental fluorosis. Maughan-Brown in 1935 and Raubenheimer in 1938 first reported a study of the occurrence of mottled enamel in South Africa (WRC, 2001). In 1941, Ockerse produced three reports on human fluorosis in various regions of the former Union of South Africa. At that time 805 areas in which dental fluorosis occurred were known (Ockerse, 1947).

In 1942, Ockerse, then a Dental Health Officer, initiated a detailed and systematic survey of the distribution of endemic fluorosis in South Africa. He carried out a national survey that covered the period, 1939-1942. In this report, he described the geographic distribution of endemic areas and linked the main cause of dental and skeletal fluorosis to the geology of those areas. Although the prevalence of dental fluorosis and skeletal fluorosis in South Africa have been recognised much earlier, sporadic and small scale studies were carried out since 1947 (Zietsman, 1991, McCaffery, 1993). No national survey was carried out since then. Like other epidemiological studies around the world, the tendency has been to concentrate on the prevalence and severity of fluorosis without much attention to the study of the distribution of high fluoride ion concentration in groundwater, the main etiological factor (WRC, 2001).

It is evident in the literature that there are various sources of fluoride. These include the ingestion of certain foods such as green tea, green vegetables like spinach, etc. (Heilman, *et al.*, 1997), the use of fluoride supplements such as various toothpastes, fluoride pills, mouthwash and drinking water. **The occurrence of fluoride levels in drinking water and the effect on dental health is the basis of this dissertation.**

The majority of dental fluorosis sufferers (mainly blacks) in South Africa live in rural areas. These people use untreated surface and groundwater as sources for drinking water. Groundwater is obtained from springs, wells and boreholes. The value of groundwater represents a strategic component of the water resources in South Africa. It occurs widely. Geographically, almost two thirds of South Africa's population depends on it for their domestic water needs (DWAF, 1997). Different studies have shown that the occurrence of dental fluorosis in the majority of cases in South Africa are related to the fluoride content of groundwater used for drinking purposes. (McCaffery, 1993;Fayazi, 1994; Du Plessis, 1995; WRC, 2001).

1.2 MOTIVATION AND PURPOSE OF THIS STUDY

The occurrence of high fluoride ion concentrations in groundwater is in most cases a natural phenomenon and constitutes a serious water quality problem in groundwater worldwide (Nair, *et al.*, 1984; M^c^Caffrey, 1993; Rao, 1997; Agrawal and Vaish, 1998). In cases where the concentrations are higher than 1,0 mg/ℓ which is the guideline in most countries, de-fluoridation techniques are used. These are expensive for most developing countries and cannot be easily implemented. Some groundwater sources in South Africa contain high levels of fluoride ion concentration levels. In many cases groundwater is the only or major source of drinking water. Effects on the teeth are visible in individuals from these areas.

In cases where fluoride levels are lower than the set standards or recommended levels for dental protection, fluoridation of water supplies is an option. Fluoridation is defined as the adjustment of the fluoride concentration of a public water supply by the addition of fluoride compounds, which meet the quality standards of the Department of Health in terms of regulation 14, set under the Health Act, (Act no.63 of 1977) in order to obtain an optimal fluoride concentration for maximum benefits, (Anon, 1998).

The awareness of excess fluoride consumption through water has however been increasing countrywide. (M[c]Caffery, 1993; Fayazi, 1994; Rudolph, *et al.*, 1995; Du Plessis, 1995; WRC, 2001). The issue of whether, and at what levels of concentration to manage the fluoride ion concentrations in South Africa's public water supplies is a contentious one. While the Department of Water Affairs and Forestry (DWAF) as the custodian of the country 's water resources, manages the fluoride levels through the criteria set in its guidelines, (DWAF, 1996) and the South African Bureau of Standards (SABS) specifications (SABS, 2001), the Department of Health proposes compulsory fluoridation of public water supplies (Anon, 1998). This has raised a number of concerns among various stakeholders and concerned parties.

1.2.1 Some concerns about the fluoridation of South African public water supplies

The application of the contents of the regulations under the Health Act has a lot of barriers:

- It has been shown by most research that the occurrence of fluoride in groundwater is in most cases a natural phenomenon. (Nair, *et al.*, 1984; McCaffery, 1993; Fayazi, 1994; Rao, 1997; Agrawal and Vaish, 1998).
- Unlike drinking water with high levels of dissolved iron and manganese, which has both colour and objectionable taste, water containing excess fluoride is colourless and tasteless. Chemical testing is required to detect its presence. For this reason, people who live in an area and drink water with high fluoride ion concentrations are not aware of the problem until fluorosis reaches advanced stages. It is of great importance for local and regional authorities to know where the areas of high natural fluoride concentrations occur such that appropriate actions in line with the legislative requirements can be taken during fluoridation. **This requires the mapping of the low and high fluoride areas in the country. This is addressed in this document.**

- The lack of adequate information that could support the fluoridation exercises is one of the aspects to be considered. Investigations (geological and geochemical) need to be carried out prior to the implementation of water supply schemes and fluoridation/de-fluoridation of the same. The removal of excess fluorides from drinking water and addition of small amounts in the case of lower levels or its absence are issues of concern to the general public as well as professionals. **The fact that there has been no detailed and systematic survey of the occurrence and distribution of fluorides at a national level in South Africa for several years indicated a need for this study.**

- There are no published South African studies on the assessment of the environmental impact of fluoridation on the natural environment. As South Africa is a water stressed country, with the establishment of the new Water Management Areas, each with its unique characteristics, the impacts will be different. A range of studies to assess possible impacts in each one of them will be required.

- Regional studies (McCaffery, 1993; Fayazi, 1994) indicate that people experiencing problems of dental caries and dental fluorosis are based in rural areas where there are no established water treatment works for groundwater. In most of these areas there is a need to clearly establish who will receive fluoride via the water supply in order to determine the viability of the policy in terms of the holistic impact.

    - Exactly what proportion of the population will get fluoride via this mechanism?
    - What population segment (risk profile from an oral health perspective) do they represent?
    - How many live in areas where it is not viable to fluoridate?
    - How many live in areas where it is not necessary to fluoridate?
    - What is the size of the population gap between those that need fluoridation and those that do not need it?
    - How long will it take to address this gap?

- Most current and recent research on fluorides in South Africa has been restricted to regional studies. (Zietsman, 1991; M[c]Caffrey, 1993; Fayazi, 1994; WRC, 2001). A national coverage or picture on the occurrence and distribution of fluorides in the country is necessary for correct decision-making concerning fluoridation/de-fluoridation of South African water supplies.

- In a country such as South Africa with extreme variations between very wet and very dry seasons, one might anticipate variations in fluoride content of the drinking water supplies in areas where this occurs. It is therefore important not only to know the levels of fluoride in groundwater destined for domestic use but also the range of variation thereof should be accurately described before fluoride supplementation. Such supplementations are usually recommended when the drinking water fluoride level is <0.7mg/ℓ (Nicholson and Duff, 1981 ; DWAF, 1996).

- The implementation of water fluoridation is influenced by social, political and economic factors. All these need to be taken into account before any water supply is fluoridated. There is a lack of accurate knowledge about water fluoridation amongst the public and this needs to be addressed (Chikte and Perez, 1995)

- There is currently no ground water quality monitoring programmes dedicated at this problem. There is also no proper ground water quality management strategy in place yet (DWAF, 2000).

The above concerns raise the following questions that need to be answered:

- Where in the country and at what concentrations is fluoride found in groundwater?
- How are people exposed to fluoride at its different concentrations?
- What health effects are caused by fluoride ingestion?
- What corrective measures can be taken to prevent endemic fluorosis?
- Are there any variations in the fluoride levels of groundwater? If so what factors contribute to this?

In this dissertation, it is attempted to answer the above questions and concerns through the following aims and objectives.

1.3 AIMS AND OBJECTIVES OF THIS STUDY

The study has three main aims:

- To determine the distribution (current and long term) of fluoride ion concentrations in groundwater sources across the country.
- To determine the extent of the incidences of dental fluorosis in selected areas.
- To investigate whether a relationship exists between high fluoride levels in groundwater and the percentage morbidity of dental fluorosis in those areas.

The objectives of this dissertation are therefore;

- To describe the distribution of fluoride in South African groundwater.
- To describe the current status of fluoride occurrence in groundwater.
- To delineate those areas with fluoride concentrations in groundwater lower or higher than the recommended limits for drinking water.
- To identify factors that may contribute to the occurrence of high fluorides in groundwater.
- To identify areas affected by dental fluorosis.
- To compare results obtained from the assessment of the water quality data and the percentage morbidity of dental fluorosis.
- To make relevant recommendations based on the results of this study.

The usefulness of this dissertation will be:

- In the identification of the areas where there are low or high fluoride levels in groundwater, that is, the delineation of areas in which the risk of fluorosis is absent (optimum levels of fluoride), less severe, or critical (fluoride levels below or higher than recommended limits). This information should allow for the most efficient utilisation of the available groundwater resources. It will contribute to correct decision making by managers especially Water Services Providers (WSPs) who have to decide whether to fluoridate or de-fluoridate water supplies, or do nothing.

- In the identification of the link between the occurrence of high fluoride levels in groundwater and the occurrence of dental fluorosis.

- In the identification of factors that affect the occurrence of fluoride ion concentrations in groundwater as demonstrated by the water chemistry, geology and historical information. This will give an insight in understanding the main aspects needed in proper fluoride management in water resources and;

- In the identification of important parameters that influence the concentration of the fluoride ion in groundwater.

The above aspects and factors are very important in the study of fluorides in groundwater, as they will give more insight and information as to how to manage the problem of high or low fluoride ion concentrations. In order to achieve the above aims and objectives, the dissertation is structured as follows:

1.4 THE STRUCTURE OF THE DISSERTATION

The structure is as outlined below

CHAPTER 1: INTRODUCTION

This chapter describes the background and motivation for the study. The approach to fluoride management in South Africa is briefly outlined and concerns are highlighted. The objectives of the dissertation are also outlined in this chapter.

CHAPTER 2: CHEMISTRY AND OCCURRENCE OF FLUORIDES IN THE ENVIRONMENT

In this chapter a detailed description of fluorides is given. This covers the occurrence and distribution of fluorides in groundwater as reflected in the literature, factors contributing to the high levels of fluoride in groundwater and beneficial effects of fluorides.

CHAPTER 3: HEALTH EFFECTS OF FLUORIDES

This chapter gives a detailed description of the health effects of fluorides. The detailed descriptions are however limited to dental and skeletal fluorosis. Fluoride metabolism is also included in this Chapter.

CHAPTER 4: RESEARCH PROCEDURES

In this chapter, general procedures used to collect, process and present the different types of data are described. Data processing is discussed.

CHAPTER 5: RESULTS AND DISCUSSIONS

Results obtained from the processing of the various data sets are presented. The way the data was analysed to get the information is described in detail. The information obtained from the results is discussed in terms of the set objectives, findings from the literature, guidelines and standards for fluoride in drinking water.

CHAPTER 6: CONCLUSIONS

In this chapter, concluding remarks are made based on the results and discussions. Reference is made to the achievement or not of the set aims and objectives.

CHAPTER 7: RECOMMENDATIONS

In this chapter, recommendations are made. The recommendations are made in the context of special reference to fluoride problems in groundwater supplies.

CHAPTER 2: THE CHEMISTRY AND OCCURRENCE OF FLUORIDES IN THE ENVIRONMENT

2.1 INTRODUCTION

The problem of high-fluoride ion concentrations in groundwater is one of the most important health-related, geo-environmental issues in many countries including South Africa. It is therefore important to manage fluoride at acceptable levels in our water resources. For this to happen, there must be proper understanding of the occurrence, factors that contribute to the release of fluoride into groundwater, influence of the fluoride ion concentration once it is in groundwater and hence the distribution of different levels of fluoride in groundwater. In all this, the understanding of the chemical characteristics of groundwater related to fluoride occurrence is critical.

The need to understand these aspects and achieve the aims and objectives of this study as outlined in **CHAPTER ONE** prompted this literature study. Included in this chapter are the following:

- **The chemistry of fluoride**
- **The occurrence of fluorides**
- **Factors that affect the occurrence of fluoride in groundwater**
- **Beneficial uses of fluoride**

2.2 THE CHEMISTRY OF FLUORIDE

Due to the very pronounced electron affinity of the fluorine atom, fluorine is capable of interacting with almost every element it comes in contact with (DWAF, 1996). It is the most electronegative of all the elements and cannot be oxidized to a positive state. It is not found in a free state in nature, but always in a combination with chemical radicals, elements or other as fluoride compounds. Fluorine forms compounds with every element except helium, neon and argon. Polyvalent cations such as that of aluminium, iron, silicon and magnesium form stable complexes with the fluoride ion. Sodium fluoride (NaF), sodium silicofluoride (Na_2SiF_4) and hydrofluosilicic acid (H_2SiF_6) are the most common and frequently used fluoride chemicals.

2.2.1 Natural Waters

In natural waters, fluorine normally occurs as the fluoride ion, F^-. Fluoride is thought to be one of the main ions that allow the solubilisation of beryllium, scandium, niobium, tantalum and tin. Most simple compounds of F^- are readily soluble in water (WRC, 2001). The E_h and pH conditions of F^- speciation are shown in Fig. 1 below. It is noted that under conditions in which water is stable, F^- usually exists as the monovalent ion, F^-. At a pH below 3.5, F^- in solution may occur in the HF form (Thompson, 1994). The close similarity in size and the equivalence of the charge of OH^- and F^- causes interference when a fluoride ion selective electrode is used for water analysis (WRC, 2001).

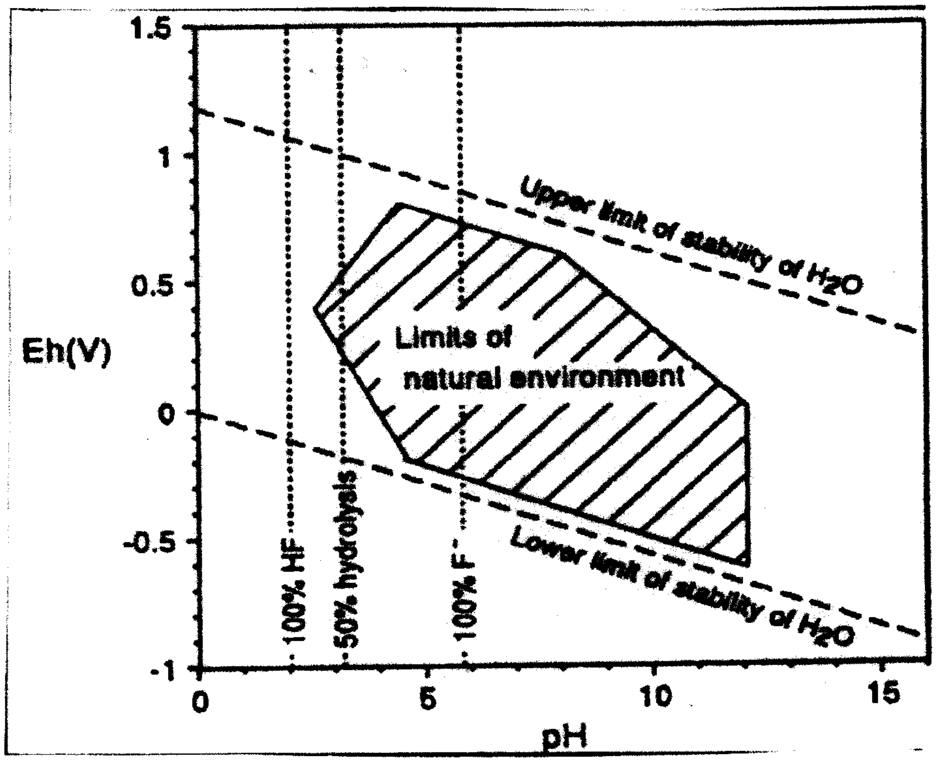


Fig 1: E_h-pH equilibrium diagram for the system F-H_2O at 25°C and for total fluoride concentration less than 2000mg/ℓ. (WRC, 2001)

The fluoride ion reacts readily with the calcium ion to form CaF_2, which is reasonably insoluble and can be found in sediments (DWAF, 1996). Where phosphate is present, an even more insoluble apatite or hydroxy apatite may form. Fluoride also reacts very readily with aluminum, a process that is made use of in the removal of fluoride from water (WRC, 2001). It forms complexes such as $(AlF_6)^{3-}$ or AlF^{2+}. The formation of these complexes takes place rapidly, at low or high pH and temperature of groundwater and their formation can be regarded in the hydrogeological context as an equillibium process (Plankey and Patterson, 1986). The formation of these complexes depends on several other factors such as complex stability constant, the concentration of the fluoride ion in solution and complexing species (Rao, *et al.*, 1993).

2.2.2 Mineral - Aqueous Fluoride Interactions

Ionic compounds of fluoride dissolve in water and these are believed to be the cause of fluoride release into groundwater. The dissolution of other F^- bearing alumino silicate minerals has also been reported (WRC, 2001).

During the mineralization of various fluoride rich minerals, solubility plays an important role. Table 1, below shows the solubility products (Ksp) values of some minerals relevant to the chemistry of groundwater (Gaciri and Davies, 1993)

Table 1: Solubility products for some minerals

Mineral	**Ksp**	**Temp.^{0}c / pH**
Fluorite (CaF_2)	3.4×10^{-11}	18
Calcite ($CaCO_3$)	1×10^{-8}	25
Aragonite ($CaCO_3$)	1×10^{-8}	25
OH^- apatite	2.6×10^{-45}	18, pH = 7.0
OH^- apatite	2.3×10^{-41}	40, pH = 7.4
Selaite (MgF_2)	6.4×10^{-9}	27
Halite (NaCl)	38 or $1 \times 10^{1.58}$	25
Siderite ($FeCO_3$)	$1 \times 10^{-10.5}$	25
Magnesite ($MgCO_3$)	1×10^{-5}	25
Dolomite	$1 \times 10^{-16.7}$	25

The concentrations of fluoride in groundwater have been shown to be limited by the mineral 's solubility especially fluorite, such that in the presence of 10^{-3} M of calcium, the fluoride ion concentration is limited to 3,1 mg/ℓ of fluoride. It is therefore the absence of calcium in solution, which allows higher concentrations to be stable (Edmunds and Smedley, 1996). High fluoride ion concentrations may therefore be expected in groundwater in calcium-poor aquifers and in areas where fluoride-bearing minerals are common.

An experiment carried out by Rao (1997) showed that the concentration of the fluoride ion in aqueous media drops with increasing bicarbonate content. The same solubility experiments carried out with fluorapatite showed an increase in the fluoride ion concentration. The results are as shown in Table 2, below.

Table 2: Solubility of fluorite, CaF_2 in the water containing $NaHCO_3$. (Rao, 1997)

Sample	**Concentration of ions (mg/ℓ)**		**Fluoride present in solution (mg/ℓ) after**		
	Na^+	**HCO_3-**	**2 days**	**10 days**	**30 days**
1	0	0	5,6	7,3	7,8
2	47	125	5,8	7,5	7,8
3	94	250	7,0	7,8	8,5
4	188	500	9,5	12,0	14,0
5	376	1000	15,0	17,0	20,0

The dominance of sodium bicarbonate waters in weathered rock formations has been found to accelerate the dissolution of CaF_2 and hence the release of fluoride into groundwater in the course of time (Rao, 1997). This experiment shows another mechanism by which alkaline solutions can mobilize F from rocks. It can be explained by the following equations,

$$CaF_2 + Na_2CO_3 = CaCO_3 + 2Na^+ + F^-$$

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + F^- + H_2O + CO_2$$

When alkaline waters come in contact with rocks, they can dissolve fluoride with simultaneous precipitation of calcite. (Rao, *et al.*, 1993). The fluoride ion concentrations of groundwater can thus reach higher levels than possible during a single weathering-evaporation cycle. The potential for dissolution or precipitation of a specific mineral in an aqueous solution has also been found to depend on the mineral's solubility and the composition of the aqueous solution. The Saturation Index (SI) defined by Langmuir measures this potential.

SI = log (^{IPA}/KT), where IAP is the ion activity product in the aqueous solution

Or Saturation percentage (SP)

SP = (IAP/KT) X 100 where K, is the equilibrium constant at temperature T

SI = O, SP = 100, indicates an aqueous solution in equilibrium with respect to the mineral.

SI < 0, SP < 100, indicates under-saturation of the solution with respect to the mineral and the tendency to dissolve.

SI > 0, SP> 100, indicates super saturation of the solution with respect to the mineral indicating thermodynamically favourable conditions for precipitation of the mineral.

It has also been established that while the fluoride ion concentration in groundwater is inversely related to Ca^{2+}, it is positively related to Na^+, HCO_3^-, EC, PO_4^{3-} and other ions. These relationships are best obtained for fluoride concentrations of 1,0–3,4 mg/ℓ. (Rao, 1997).

Compositional characteristics of some waters include high alkalinity (pH generally greater than 7) and richness in the components Na, K, HCO_3^-, CO_3^{2-} as well as Cl^- and F^-. These species have high solubility in water. Fe has low solubility because it is precipitated from alkaline water. Ca and Mg are low, as they are precipitated as carbonates and hydroxides respectively. Only limited incorporation of F is permitted in the $CaCO_3$ structure, such that there is always a net balance of F in solution. The higher solubility product of $CaCO_3$ (Ksp = 1×10^{-8}) favours its precipitation over CaF_2 (Ksp = $3{,}4 \times 10^{-11}$).

$$CaCO_3\,(s) \quad + H^+ \quad + 2F^- \quad = \quad CaF_2\,(s) \quad + \quad HCO^-_3$$

Fluorite.

$$K_{Ca\text{-}F\text{-}} = \frac{(HCO^-_3)}{(H^+)*(F^-)^2}$$

Depending on pH, an increase or decrease in bicarbonate concentration/activity will be accompanied by a corresponding increase or decrease in the concentration of fluoride ions. This is due to the formation of hydrofluoric acid, HF.

The fluoride ion forms complexes with elements such as Al, Mg, Fe and Be and this may be an important factor which determines the total concentration of fluorite which dissolves in groundwater. The calcium ion also complexes significantly with the carbonate and sulphate ions. This can increase the solubility of fluorite and hence its mineralization. This complexation has the effect of reducing free calcium and fluoride activities, thereby increasing the tendency of fluorite to dissolve. Silicates complexation is also possible but only in the acidic range (Rao, 1997).

2.2.3 In Soil

Soils adsorb F^- from dilute and concentrated solutions and this process is being used industrially (Ginster and Fey, 1995). It has been noted that the fluoride ion mobility depends on soil type, pH of the system and fluoride ion concentrations. Retention of F^- in the soil system is favored in acidic sediments containing clays and poorly ordered hydrous oxides of aluminum. Jinadasa, *et al.,* 1993 investigated the F^- adsorption onto the surface of goethite (Fe0.0H). They found that fluoride adsorption is minimal above pH 7 and increased with decreasing pH, being greatest at pH 4. In 1996, Meeusen and his colleagues concluded that the behaviour of F^- in a soil profile was mainly determined by adsorption onto the metal oxide and hydroxide surfaces, specifically with goethite and gibbsite.(Meeusen, *et al.*, 1996)

2.3. OCCURRENCE OF FLUORIDES

2.3.1 General

Fluorine is the lightest element in the halogen group. It is the 14^{th} most abundant element in the lithosphere. Fluorine is rarely found in its elemental state in the earth's crust. It usually forms ionic bonds with most elements of the periodic table (Gaciri and Davies, 1993; WRC, 2001,). These compounds are called fluorides. Bonding with anions of groups VA, VIA and VIIA (apart from P, As and Bi) does not occur because of the high electro-negativity of fluorine. (WRC, 2001).

2.3.2 Occurrence of fluorides in South Africa

2.3.2.1 In Rocks

Fluorides are found in varying amounts in practically all the geological formations, especially in most igneous rocks. (M^{c}Caffrey, 1993; Fayazi, 1994). Fluorides occur most abundantly in nature as fluorspar or fluorite (CaF_2) and crinoline, a fluoride of aluminum and sodium, (Na_3AlF_6) (Rawhani, 1986). Fluorspar contains 48.9% fluoride and cryolite, 54.40% (Oscerse, 1947). Cryolite occurs to a lesser extent than fluorspar in South Africa. Various fluorosilicates $(SiF_6)^{2-}$ have also been found. Fluorspar is found mostly in phosphate bearing rocks but it is also widely associated with granite and dolomitic formations. The majority of these deposits, however, are in small and scattered pockets normally found in the granite of the Bushveldt type, the dolomite and the limestone deposits of the Highveldt (Rawhani, 1986). South Africa's economically most significant deposits of fluorspar occur in dolomites of the Malmani subgroup (Transvaal sequence) of the North-West Province and Felsic members of the Bushveld Complex (Munzhelele, 1998). Minor occurrences are known in KwaZulu Natal. Fluorspar deposits are also found in some of the alkali and carbonatite complexes in the Northern Province, which are of the post Bushveld age. South Africa's reserves of fluorspar are the world's second largest (Munzhelele, 1998).

On the farm Witkop, in the North-West Province, the deposits consists of a large flat vein beneath a thin layer of shale near the surface which gives way to a pipe-shaped body with angular frameworks of dolomite enclosed in fluorspar and large number of irregular branching veins developed along cracks and fissures (Mohlahlo, 2000). The deposit of the Vergenoeg Mine, near Pienaarsrivier in the Northern Province grades 40% of CaF_2 and occurs with abundant iron oxide in a massive deposit in felsite (Mohlahlo, 2000).

The most important geological formations in which fluorides may occur in other provinces like the Cape Provinces are the Karoo sediments, volcanics, the younger granites and felsites, the older granites and gneiss. These include the formations which are built of fragments of the above mentioned rock formations such as the Dwyka Tillite or the base of the Karoo sediments and the basalt beds of the Crestaceous system (Oscerse, 1947, Fayazi, 1994).

The following table gives the total fluoride concentrations recorded in some rocks in South Africa:

Table 3: Total fluoride concentrations recorded in some rocks in South Africa

Rock	**Area**	**F content, mg/kg**	**Reference**
Lebowa granite	North-West Province	1570	McCaffrey, 1995
Pilanesberg (whole rock mean)	North-West Province	27000	McCaffrey, 1995
Amphibolite	North-West Province	104 - 1400	McCaffrey and Willis, 2001
Gneiss	North-West Province	240 - 2800	McCaffrey and Willis, 2001
Phosphate rock	North-West Province	10400 - 42000	McCaffrey and Willis, 2001
Dolomite	North-West Province	110 - 400	McCaffrey and Willis, 2001

2.3.2.2 In Minerals

Common fluoride minerals are fluorspar and fluorapatite, a calcium fluorophosphates mineral. In South Africa the minerals, which contain variable amounts of $F^-$are as listed below: (Ockerse, 1947; McCaffrey, 1993; Fayazi, 1994, and WRC, 2001).

(i) Fluorspar (CaF_2)
(ii) Flourapatite ($3Ca_3P_2C_8CaF_2$)
(iii) The various micas
(iv) The amphiboles
(v) Tourmalite
(vi) Topaz (Al_2) (SiO_4) (OH, F)$_2$

(vii) Fluocerite (Cerium Lanthanum fluoride)

(viii) Apophyllite

(ix) Bultontenite

(x) Zunyite (orthosilicate of aluminum)

(xi) Ephesite

Others of importance include various fluorosilicates and mixed fluoride salts such as cryolite (Na_3AlF_6)

Table 4: Occurrence and Chemical composition of some minerals found in South Africa (Ockerse, 1946, GSSA, 1986, Mohlahlo, 2000, WRC, 2001)

Mineral	**Formula Composition**	**Occurrence**
Fluorite (Fluorspar)	CaF_2	Malmanie, Witkop and Buffelshook usually found in the Bushveld Complex Associated with red granite. Was mined in the Pilanesberg area, North -West Province on the farm Tooyskraal, 43.2km west of Warmbaths, Ruigtepoort, 48 km South-West of Warmbaths, Grobbelaars Hoek, ± 112 km North-West of Potgietersrus and Buffelsfontein, 4.8km North-West of Naboom-Spruit. Also Found in alkaline intrusions North and Northeast of Pretoria. Hlabisa in KwaZulu Natal.
Fluorapatite	$3Ca_3P_2C_8CaF_2$ 92.26% Ca_3 $(P0_4)_2$ 7.74% CaF_2	Spitkop farm, Eenzaam in Sekukuniland, Wallamansthal, 28.8km Noth-East of Pretoria. In dolerite Deposits.
Various micas Muscovites (White mica) Biotites (Black Mica)	Silicates of Al, K and H_2 with Fe, Mg, Na, Li	White micas, Muscovites in the Letaba District, North-West Province , Namaqualand. Micas form a constituent of all granites, fluorides are present in all granites in South Africa. Is a constituent of many metamorphic rocks, also in sediments.
Amphiboles	Silicates of Fe, Mg, Ca, and some-times K and Sodium	Namaqualand, North-West Province
Topaz	Al_2 Si 0_4F_2	Occurs in igneous rocks, granites. Bushveld Igneous Complex in the deposits on the farm Vlaklaagte, 86.4km North-East of Pretoria
Fluocerite	R_20F_4(R=Ce, la, Di)	Springbok Flats, North - West Province

2.3.2.3 In Soils

Fluorides in soils in some parts of South Africa are usually derived from the weathering of the underlying fluoride-bearing rocks (Fayazi, 1994). Fluorides are found in soils with high contents of phosphates, clay minerals, and colloids at its lowest concentration in light, sandy soils. (WRC, 2001). It is generally depleted in soils relative to the parent fresh rock. This is as a result of dissolution, but the behaviour of fluorides during weathering is complex. The controlling factors evident from the literature appear to be soil type, calcium and phosphorus content including soil pH.

2.3.2.4 In Water

Traces of fluorides are present in many waters; higher concentrations are often associated with underground sources. As fluorides occur in nearly all-geological formations in South Africa, it is not surprising to find them present in variable concentrations in both surface and groundwater in many areas. Typically, the concentration of fluoride in:

- Unpolluted surface water, is approximately 0,1 mg/ℓ
- Groundwater is commonly up to 3 mg/ℓ, but as a consequence of leaching from fluoride containing minerals to groundwater supplies a range of 3-12 mg/ℓ or higher may be found (DWAF, 1996).
- Seawater, the fluoride ion concentration is found approximately at 1,3 mg/ℓ (DWAF, 1996).

2.3.2.4.1 In South Africa

South Africa is among the noted in the world for experiencing high levels of fluoride ion concentrations in groundwater on a regional scale. Several researchers have noted the high F^- content of certain groundwater in South Africa (Table 5). Ockerse in 1946 measured rock, soil and groundwater concentrations of F^- in an attempt to understand the causes of endemic dental fluorosis. His study covered the whole of South Africa, then, the former Union of South Africa but unfortunately gave the Western Bushveld only superficial attention (WRC, 2001). He did, however, single out the Pilanesberg, Warmbaths and Pretoria Saltpan as areas with endemic dental fluorosis deserving greater investigation. He suggested that fluoride in groundwater of the Springbok flats came from the Ecca formation and suggested fluorapatite as the source. Fayazi, 1994 suggested that the Karoo sedimentary strata contained fluorite derived from the surrounding Bushveld Granites during episodes of arid erosion.

In South Africa, fluoride distribution, show that groundwater with a fluoride content greater than the recommended level of 1,0 mg/l is situated in areas underlain by the Karoo sedimentary rocks (Claren-Sandstones - TRC, Irrigasie sediments, P-TRC and Ecca Shales - Pe). The table below summarises some of the findings.

Table 5: F content recorded for some boreholes in South Africa (Fayazi, 1994)

Farm name and Number	Borehole number	Borehole depth (m)	H - number	F in mg/l	Geology
Alexanderfontein 626KS	7	274,3	91405725	11,11	P-tri/pe, Tillite
Alexanderfontein 626KS	2	213,4	81410539	13,09	Jd
Alexanderfontein 626KS	5	300	72010657	10,80	Ptri/PePe Tillite
Bouw lust 660KS	1	97,5	91405762	8,22	Pe/Conglome rate
Buiten post 656KS	6	85,0	81410369	19,18	Pe/Vma
Groote post 661KS	2	116	91405750	10,72	Pe/Jd
Groote post 661KS	5	61,0	814106485	12,84	Jd
Klaver Valley 671KS	6	61,0	81410440	11,12	Pe/Bedrock
Minerva 628KS	4	213,4	72011085	25,40	P-Tri/Pe/Bedrock

P- Tri: Irrigasie sediments (mudstone / siltstone)
Pe: Ecca shale
Jd: Dolerite dyke / silt
Vma: Sandstone

2.3.2.5 In the Biosphere

In plants, fluoride is mostly stored in the leaves, after translocation from the root system or directly from absorption from the atmosphere. The availability of fluorides to the root system is decreased by increases in the pH, phosphate, calcium, clay and organic matter content of the soil (WRC, 2001). Typical fluoride concentrations in non-accumulator plants are below 20-mg/kg dry weight.

2.3.2.6 Fluorides in the atmosphere

Due to dust, industrial production of phosphate fertilisers, coal ash from the burning of coal and various industries, fluorides are widely distributed in the atmosphere. Inhaling dust rich in fluorides is as dangerous as consuming fluoride containing food, water or drugs. Most plants obtain fluoride through the polluted atmosphere. However, air is typically responsible for a small fraction of total fluoride explosure (USNRC, 1993). In non-industrial areas, the fluoride concentration in air is typically quite low (0,05 to 1,90 mg F^{-}/m^3 (WHO, 1986). In areas where fluoride-containing coal is mined or phosphate fertilisers are produced and used, the fluoride in the air is increased leading to increased exposure by the inhalation route. High levels of atmospheric fluoride occur in areas of Morocco and China (Haikel *et al.*, 1986). In some provinces of China, fluoride concentrations in indoor air ranged from 16 to 46 mg/m^3 owing to the indoor combustion of high-fluoride coal for cooking, drying and curing food (WHO 1996). Indeed, more than 10 million people in China are reported to suffer from fluorosis related to the burning of high fluoride coal. (Guo and Wang, 1998)

2.3.2.7 In food

Ingesting food and drinking water containing fluorides over a period of time is likely to result in toxic manifestations. It is well recognised that consuming fluoride contaminated food or water for a period of 6 months to a year is adequate to have ill effects on the health especially during childhood. **The details on the health effects of fluorides on human health are given in Chapter three of this dissertation.** Virtually all foodstuffs contain at least traces of fluoride.

All vegetation contains some fluoride that is absorbed from soil and water. Vegetables and fruits normally have low levels of fluoride, (0,1–0,4 mg/kg) and that typically contributes to little exposure. (Heilman, *et al*., 1997). However higher levels of fluoride have been found in barley and rice (about 2 mg/kg) and taro, yams and cassava have been found to contain relatively high fluoride levels (WHO, 1986). High concentrations in tea can be 3-300 mg/kg (average 100 mg/kg), so 2-3 cups of tea contain approximately 0,4-0,8 mg (WHO, 1984). In areas where water with high fluoride content is used to prepare tea, the intake via tea can be several times greater. In general, the levels of fluoride in meat have been found in the range of 0,2–1,0 mg/kg. In fish levels of (2–5 mg/kg) have been recorded (Heilman, *et al*, 1997).

Seafood contains significantly higher fluoride concentrations compared to freshwater food. Fluoride accumulates in bone and the skeleton of canned fish such as salmon and sardines (Hammer, 1986). Fish protein concentrates may contain up to 370 mg/kg fluoride. However, even with a relatively high fish consumption in a mixed diet, the fluoride intake from fish alone would seldom exceed 0,2 mg of F^- per day (WHO, 1986).

Dietary studies have shown that fish accumulate fluoride in hard tissues and in parts of South East Asia this resulted in some human populations having a high fluoride diet. Those parts of fish in contact with the water, such as scales, fins and gills, have high fluoride levels. Skin is very high in fluorides and predators consuming the whole fish are subject to much higher fluoride levels than man who often removes skin first (Heilman, *et al.*, 1997).

Dairy feed and mineral supplements may contain high levels of fluoride, up to 200 mg/kg, though most are fewer than 30 mg/kg. Cows may thus get more than their daily dose of fluoride from this source before water and forage are even considered. Bone meal supplements can be very high in fluoride since cattle grazing contaminated pastures may accumulate 100 mg fluoride/kg of bone, the normal level is 15 mg fluoride/kg. Results from a detailed study on dietary sources are summarised below (Heilman, *et al,* 1997).

Table 6: A summary of dietary sources of fluoride as summarised by Heilman, *et al*, 1997

Food source	**State**	**Quantity (g/other)**	**F content mg**
Green tea	Cooked	6 cups	160-660
Ham	Baked	100g	1.7
Greens	Raw	100g	1.5
Chocolate cake	Baked	100g	1.3
Fish	Fried	100g	1.3
Tooth paste	-	100g	1000
Mouth wash	-	½ a teaspoon	4000
Gel treatments	-	100g	13000
Oatmeal	Cooked	100g	10.6
Rice Krispies	Krispies	100g	5.9
Cottage Cheese	-	100g	5.0
Coffee	-	100g	5.0
Noodles	Cooked	100g	4.6
Mashed potatoes	Cooked	100g	4.3
Minestrone soup	-	100g	4.1
Spinach	Cooked	100g	3.7
Rice	Cooked	100g	3.5
Spaghetti sauce	-	100g	3.3
Cheerios	Cooked	100g	3.3
Peas	Cooked	100g	3.0
Toast	-	100g	2.7
Sausage	-	100g	2.5
Potatoes	Boiled	100g	2.5
Pork, roast	Roasted	100g	2.1
Whole-wheat bread	-	100g	1.7

N.B- none of the above values were experimentally verified in this study

2.4 FACTORS THAT CONTRIBUTE TO THE OCCURRENCE OF HIGH FLUORIDE IN GROUNDWATER

The incidences of high fluoride ion concentrations in groundwater has been attributed to various causes:

- High F content of aquifers
- Low groundwater flow rates
- Semi-arid climate increasing potential evaporation
- High pH waters
- Weathering of alkaline volcanic rocks rich in F
- Fluorspar mineralization and occurrences of rock phosphate deposits
- Granites, gneisses and other crystalline rocks having many fluoride bearing minerals as their essential and accessory mineral composition
- Residual soils including micaceous sand
- Variation in soil texture
- Industrial activities and use of pesticides and insecticides (less common and rare in most cases).
- Various volcanic activities (Rao, *et al*, 1993, Fayazi, 1994, Rao, 1997, Agrawal and Vaish, 1998, WRC, 2001).

In the majority of cases, the incidence of high fluoride ion concentrations in groundwater is mainly a natural phenomenon, influenced basically by the local and regional lithological setting, mineralization characteristics and hydrogeological conditions. (Fayazi,1994; Rao, 1997, Agrawal and Vaish, 1998). The continuous and long term weathering and leaching mainly by moving and percolating water play the important role in the release of fluoride from minerals, soils and rocks into groundwater. (Fayazi, 1994, Agrawal and Vaish, 1998). In South Africa, it has been confirmed that the general distribution of the fluoride ion in "problem areas" is controlled by the geochemistry of the rock in which the groundwater is encountered. (M^cCaffrey, 1993, Fayazi, 1994;WRC, 2001). Lithological controls suggest that the cause of high fluoride concentrations in groundwater is due to the dissolution of fluoride bearing minerals in bedrock and soil (M^cCaffrey, 1993). The above factors can be classified into three major classes as described below:

Class III

Climatic conditions (comparatively temperatures and precipitation favour effective chemical weathering (Nanyaro, *et al.*, 1984). The composition of the waters therefore reflects partly the lithology of the drainage basins. During arid episodes and the process of erosion, weathered products derived from granitic rocks containing fluorite in the groundwater at this point. (Fayazi, 1994). Groundwaters associated with dolerite dykes and silts, which have intruded sedimentary rocks often, have a relatively high fluoride content.

It has been found that higher fluoride concentrations are obtained in discharged area than in recharge areas, with a trend of fluoride enriched along the direction of flow. These features have been attributed to the smaller quantities of dissolved solids in the recharge areas. (Gaciri and Davies, 1993).

Industrial processes also contribute to the presence of fluorides in groundwater. Quantities of fluorides pour into the atmosphere each year from aluminium smelters, phosphate processing, coal burning, manufacturing of steel, fluoride compounds, bricks and glass products. Such industries that use fluorides either as raw materials in the manufacturing process or in which they arise as by-products or may even be end-products include enamel, pottery, welding, refrigeration, rust removal, oil, refinery, plastic, pharmaceuticals, fertilizer, automobile and toothpaste industries. However, this route is less important at the moment as the most affected and vulnerable are plants and livestock.

- Factors relating to the availability of fluorides that pass into the hydrological system, namely volcanic activity associated with rift formation and the composition of the volcanic rocks and other types of rocks.

- Factors determining the residence times of dissolved fluorides in the waters, i.e., chemical reactions especially involving the species, Ca^{2+} and F^-, among others.

- Factors of generally lesser significance may however become locally important, these include the injection of fluorides into the hydrological system by industrial operations, for example, fluoride mining and introduction of fluoride through atmospheric precipitation and dissolution of salt crusts. Examples under each class are described below.

Class I

Volcanism is an important factor determining fluoride content of the natural waters (Gaciri and Davies, 1993). Four major geological systems are evident: metamorphic rocks of Precambrian age, sedimentary rocks of Carboniferous to Createaceous age, Tertiary and Quartenary volcanics and Unconsolidated Tertiaty and Quarternary sediments. It is the chemical leaching, weathering of these rocks and their associates that contribute to the release of fluoride into groundwater. Waters from these volcanic rocks have shown relatively high fluoride content, up to 180 ppm or more. The fluoride content of amphiboles from metamorphic rocks worldwide varies from 30 to 21 400 mg/kg (Gaciri and Davies, 1993). In this process the solubility of the mineral plays an important role. **(See 2.2.2 above)**

Class II

Besides geological changes, which result in changes in recharge composition and mixing, several chemical processes have been identified as being important in controlling the major ion chemistry. Other existing minerals in the subsurface and other major and minor ionic constituents of groundwater may affect the dissolution characteristics of minerals, for example fluoride, CaF_2, (Rao, 1997).

CHAPTER 3 HEALTH EFFECTS OF FLUORIDES

3.1 INTRODUCTION

Many water quality assessment and epidemiological studies of possible adverse effects of long-term ingestion of fluoride via drinking water have been carried out. These studies clearly establish that fluoride primarily produces effects on skeletal tissues (bones and tissues) (Chen, 1993; M^{c}Caffrey, 1993, DWAF, 1996; Ogera, 1997;Guo and Wang, 1998; Muller, *et al.*, 1998). Low concentrations provide protection against dental caries, especially in children. This protective effect increases with concentration up to about 2mg/ℓ of drinking water. The minimum concentration of fluoride in drinking water required to produce this effect is approximately 0,5 mg/ℓ (WHO, 1994; Du Plessis, 1995). High fluoride concentrations exert a negative effect on the course of metabolic processes and consequently individuals may suffer from dental fluorosis, skeletal fluorosis, osteoporosis and non-skeletal manifestations or a combination of these.

Since the use of groundwater discussed in this study is mainly for drinking purposes, the effects discussed in this study will be limited to those effects caused by ingesting fluoride via drinking water. The scope of this dissertation is limited to the effect on dental health. In order to understand these effects fluoride metabolism will first be discussed.

3.2 FLUORIDE METABOLISM

3.2.1 Absorption

Approximately 75–90% of ingested fluoride is absorbed. (DWAF, 1996) In an acidic stomach, fluoride is converted into hydrogen fluoride (HF) and up to about 40% of the ingested fluoride is absorbed from the stomach as HF. (Clair, *et al.*, 1994). High stomach pH decreases gastric absorption by decreasing the concentration of HF. Fluoride not absorbed in the stomach is absorbed in the intestine and is unaffected by pH at this site. (Whitford, 1997). Relative to the amount of fluoride ingested, high concentrations of cations that form insoluble complexes with fluoride (e.g. calcium, magnesium and aluminium) can markedly decrease gastrointestinal fluoride absorption (Whitford, 1997). When water-containing fluoride is consumed, some fluoride is retained by fluids in the mouth and is incorporated onto the teeth by surface uptake (topical effect). The rest enters the stomach where it is rapidly adsorbed by diffusion through the stomach walls and intestines. Fluoride enters the blood plasma and is rapidly distributed throughout the body, including the teeth (systemic effect).

3.2.2 Distribution

Once absorbed into the blood, fluoride readily distributes throughout the body, tending to accumulate in calcium rich areas such as the bone. This includes the teeth (WHO, 1996). Because of the systemic effect, the fluoride ion is able to pass freely through all cell walls and is available to all organs and tissues of the body. Distributed in this fashion, the fluoride ion is available to all skeletal structures of the body in which it may be retained and stored in proportions that generally increase with age and intake. Under certain conditions, plasma fluoride levels provide an indication of the level of fluoride in the drinking water consumed. USNRC, 1993 notes that, when water is the major source of fluoride intake, some plasma fluoride concentrations of healthy young or middle-aged adults expressed in micromoles per litre are roughly equal to the fluoride concentrations in drinking water expressed as milligrams per litre (USNRC, 1993).

3.2.3 Excretion

Fluoride is excreted via urine, faeces and sweat (WHO, 1996). Most is excreted via urine with faeces and sweat playing only a minor role. Urinary fluoride clearance increases with urine pH due to a decrease in the concentration of HF. Numerous factors, for example, diet and drugs can affect urine pH and thus affect fluoride clearance and retention (USNRC, 1993).

3.3 BENEFICIAL USES OF FLUORIDES

The beneficial attributes of fluorides to human health have been known for some years (WHO, 1970; WHO, 1984a; Hammer, 1986; Pontius, 1991; WHO, 1994; Du Plessis,1995). When ingested at specific doses, the fluoride ion is beneficial to both bone and dental development in human beings. The beneficial plateau is generally between 0,5 and 2,0mg/l depending on average ambient temperatures which control fluid intake and thus the total dose/day. The total daily intake of fluoride from food is about 0,2-0,5mg, which is only 10-15% of the desirable dose (Pontius, 1991, Boyle and Chagnon, 1995). It has been noted that the fluoride ion is a normal constituent of all diets and at correct concentrations it has beneficial effects in preventing dental caries (Pontius, 1991).

Dental caries is a disease caused by specific bacteria harboured in dental plaque, fermenting carbohydrate to produce acid that can demineralise tooth enamel (Hammer, 1986). If this demineralisation is allowed to continue, the enamel is penetrated permitting bacterial invasion and eventual loss of the tooth by decay in the absence of restorative dental care. It can be reduced by the use of fluoride products. The level of dental caries (measured as the mean number of decayed, missing or filled teeth) falls from seven at a fluoride concentration of 0,1mg/l to around 3,5 at a fluoride concentration of 1,0mg/l. As the fluoride ion concentration increases further (up to 2,6mg/l) dental decay continues to fall, but only slightly (Dean, 1942; USPHS, 1991). The optimal level of fluoride for a temperate climate has been found to be around 1,0mg/l. This concentration seems to be associated with a substantial resistance to tooth decay but with only a small and cosmetically insignificant increase in the prevalence of dental fluorosis. For an individual, other effective methods for the prevention and control of caries are to restrict intake of dietary sugars and plaque control by flossing and brushing.

Other beneficial uses, which are not discussed in detail in this survey, include various industrial uses, adjustment of fluoride levels in water supplies, termed water fluoridation. A brief discussion on fluoridation is given in **Chapter one**. The benefits of water fluoridation have been found to be mostly in children. These include:

- The reduction of the likelihood of dental abscesses,
- The reduction of the risk of toothache,
- The reduction of the need for tooth extractions and general anaesthesia and
- the reduction of the cost of dental treatment.

3.4 EFFECTS OF FLUORIDES ON HUMAN HEALTH

3.4.1 General

The effects on skeletal tissues (bone and teeth) caused by the consumption of drinking water rich in fluorides are well documented. (Driscoll, *et al.*, 1985; Hammer, 1986; Brouwer, *et al.*, 1988, Du Plessis, 1995). Both deficient and excessive amounts of fluoride may be harmful to human health. Where the concentrations are low, tooth decay results and where they are high, dental fluorosis (mottling of tooth enamel may occur). (Gosselin, *et al.*, 1999).

3.4.2 The Significance of low fluoride ion concentrations in drinking water supplies

In 1938, Dean presented information, which demonstrated that dental caries is less prevalent when mottled enamel occurs (USPHS, 1991). From his studies a hypothesis evolved: Approximately 1,0mg/l of fluoride ion is desirable in public waters for dental health. At decreasing levels, dental caries became a serious problem. This dental caries-fluoride hypothesis has served as the basis for programs of supplementing public water supplies having low fluoride levels with fluorides to bring the concentration up to about 1mg/ℓ. The main significance of the existence of low fluoride levels in water supplies is the development of dental caries. However fluoride may give rise to mild dental fluorosis at drinking water concentrations between 0.9 and 1,2 mg/ℓ. This has been confirmed in a series of studies carried out in China. (Chen, *et al.*, 1993; Clair, *et al.*, 1994). These studies showed that, with drinking water containing 1,00 mg/ℓ of fluoride ion concentration dental fluorosis is detected in some populations.

3.4.2.1 Dental Caries

Dental caries is the commonest disease that is affecting mankind and produces a permanent breakdown of tooth substance (Muller, *et al.*, 1998). It happens when bacteria on the surface of the teeth ferment carbohydrates to produce acids that then destroy the hard, calcified tooth tissue. Fluoride interferes with the metabolism of bacteria, and inhibits the production of the acid by decay-causing bacteria. (Pontius, 1993). This results in a change in the population of bacteria in dental plaque.

In South Africa, tooth decay is one of the most common health problems and leads to loss of working and schooling days as a result of pain and suffering (Muller, *et al.*, 1998). Caries affects 90 to 93% of the South African population (Van Wyk, 1995). The fluoridation of public water supplies is aimed largely at the developing community; fluoride levels of 0,3 to 0,4 mg/ℓ will be able to reduce the incidence of caries by 56% (Carstens, 1995). The low costs of adding fluoride to water, the fact that 80% of the people in South Africa are dependant on the state, and the high incidence of caries, particularly among the developing communities makes it a moral issue to regulate fluoride levels in drinking water (Muller, *et al.*, 1998). The effects on the labour force make it an economic issue.

3.4.2.2 Remediation

In 1930s and 1940s, studies in the United States found that natural levels of 1mg/l fluoride reduced the incidence of dental caries by approximately 50% (WHO, 1994). Lifetime consumption of fluorides, whether taken systematically or used topically, significantly reduces the incidence of dental caries. (Hargreaves, 1990, Murray, *et al.*, 1991). Fluoride is essential to the development of resistance to caries and these benefits are for a lifelong duration. It reduces the susceptibility of teeth to caries by stabilising the apatite crystal of the dental enamel, making it more acid resistant and results in remineralisation of the enamel. (Pontius, 1993). Fluoride is essential from birth until the permanent teeth have been formed as it is incorporated into the tooth enamel, which is formed before the teeth erupt. In instances where water supplies have been found to be deficient in fluoride ion concentration people have resorted to water fluoridation.

3.4.2.3 Fluoridation

Water fluoridation has been defined as the deliberate adjustment (either by increasing or decreasing) of the fluoride levels of a water supply so that the greatest protection against dental caries is produced with the least risk of dental fluorosis (Pontius, 1991). But this is confusing, since fluoridation is generally understood by the public as only the addition of fluoride to drinking water supplies. The definition commonly used in South Africa is as provided in Chapter one of this Thesis, that is, the adjustment of the fluoride concentration of a public water supply by the addition of fluoride compounds, which meet the quality standards of the Department of Health.

3.4.3 The Significance of High fluoride ion concentrations in drinking water supplies

Churchill of the Aluminium Co. of America obtained substantial evidence that fluorides are the cause of mottled enamel in 1930. Churchill through spectrographic analysis, found appreciable amounts of fluoride ion in the Bauxite water supply. In collaboration with McCKay, a dentist of Colorado Springs, Colorado, studied waters from five areas where mottling was endemic and from 40 areas where it was not a problem. From these studies it was concluded that excessive fluoride levels in drinking water are the cause of mottled enamel. Their data showed that mottling did not appear unless the fluoride –ion concentration was in excess of 1mg/l and that the degree and severity of mottling increased as the fluoride level rose. (Clair, *et al.*, 1994).

In South Africa, researchers have proved in various research works that excessive fluoride causes dental fluorosis. (Oscerse, 1946; McCaffery, 1993; Du Plessis, 1995; WRC, 2001). When fluoride levels in drinking water exceed 1,5 to 2,0 mg/ℓ, dental mottling occurs, the severity of which increases with increasing fluoride concentration. (Boyle and Chagnon, 1995). High doses of fluoride interfere with carbohydrate, lipid, protein, vitamin, enzyme and mineral metabolism. The current threshold for fluoride chronic poisoning as recommended by the DWAF is 4mg/ℓ (DWAF, 1996). Skeletal fluorosis may occur when concentrations of fluoride in water exceed 3-6 mg/l and becomes crippling at intakes of 20-40 mg/day. This is the equivalent to a fluoride concentration of 10-20 mg/ℓ, for a mean daily water intake of two litres. (DWAF, 1996).

3.4.3.1 Dental fluorosis

Dental fluorosis is associated with the ingestion of high levels of fluorides. It is characterised by discoloured, brown stained or blackened, mottled or chalky white teeth. (See Fig 2 below). These effects are not apparent if the teeth were already fully-grown prior to fluoride over exposure therefore, the fact that an adult may show no signs of dental fluorosis doesn't necessarily mean that his or her fluoride intake is within the safety limit. Dental fluorosis is a clear indication of over exposure to fluoride during childhood when the teeth were developing (Driscoll, *et al*, 1985).

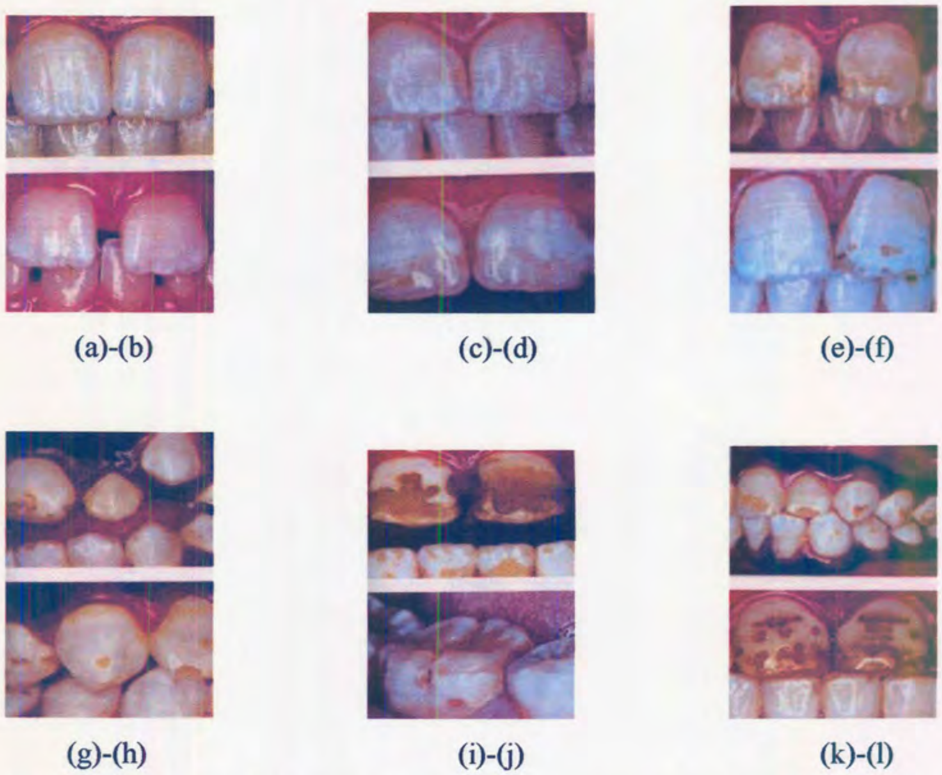


Fig 2: (a)-(b) Mild dental fluorosis, white opaque areas cover tooth surface, Brown stains starting to build up.

(c)-(d)-Very mild dental fluorosis, the tooth surfaces covered by white opaque, paper-white areas.

(e)-(f) Brown stain superimposed on white cloudy areas. Brown stain equals enamel loss

(g)-(h) severe dental decay accompanied by dental fluorosis

(i)-(j) severe dental fluorosis, chipping and large brown stains, loss of tooth structure.

(k) –(l) the enamel damage effects more teeth , unsightly and weakened teeth result. Most of enamel has been lost from tooth surface. The protective layer is gone due to dental fluorosis.

Endemic fluorosis is very high in China (Chen, *et al*, 1993; Guo and Wang, 1998). It exits in almost all provinces, municipalities and autonomous regions. According to the 1997 statistics, the population in the disease stricken areas was around 100 million, with more than 2.7 million bone fluorosis patients. There are various types of endemic fluorosis in China, one caused by drinking water contaminated with high fluorides, eating or drinking foodstuffs rich in fluoride such as green tea and the one caused by exposure to coal burning.

While there are a variety of ways of describing dental fluorosis, Dean's 1942 description is still extremely useful and widely used in epidemiological studies. (Brouwer, 1988; Du Plessis, 1995).

Table 7: Dental Fluorosis Categorisation (Dean, 1942a)

Normal	The enamel presents the usual translucent, semi-vitriform type of structure. The surface is smooth, glossy and usually of a pale creamy white colour.
Questionable	The enamel discloses slight aberrations from the translucency of normal enamel, ranging from a few white flecks to occasional white spots. This classification is used in those instances where a definite diagnosis of the mildest form of fluorosis is not warranted and a classification of "normal" not justified.
Very mild	Small, opaque, paper-white areas scattered irregularly over the tooth, but involving less than approximately 25% of the tooth surface. Frequently included in this classification are teeth showing no more than 1-2mm of white opacity at the tip of the summit of the cusps of the bicuspids or second molars?
Mild	The white opaque areas in the enamel of the teeth are more extensive but do not involve as much as 50% of the tooth.
Moderate	All enamel surfaces of the teeth are affected, and surfaces subject to attrition show marked wear. Brown stain is frequently a disfiguring feature.
Severe	Includes teeth formerly classified as "moderately severe" and "severe". All enamel surfaces are affected and hypoplasia is so marked that the general form of the tooth may be altered. The major diagnostic sign of this classification is the discrete or confluent pitting. Brown stains are widespread and teeth often present a corroded-like appearance.

Dental fluorosis is a sign of chronic fluoride poisoning in children under six to seven years of age. Unfortunately this is only seen years after the damage, which is irreversible has been done. The recommended upper limit to prevent dental fluorosis varies from region to region, as the fluoride concentration is dependent on the environmental temperatures.

3.4.3.2 SKELETAL FLUOROSIS

This has been defined as the hardening or abnormal bone density, which develops in a person as a result of drinking water with more than 3 mg/l of fluoride (Rajagopal and Tobin, 1991). Crippling skeletal fluorosis has been observed where drinking water contains over 10 mg/l (WHO, 1984a). The level of fluoride in drinking water necessary to produce crippling skeletal fluorosis can vary markedly from one region of the world to another. This has been observed in the results obtained from Senegal (Brouwer, *et al*., 1988) and the United States example (Leone, *et al.*, 1955; USNRC, 1993). Brouwer, *et al*., (1988) observed that of the 42 individuals in Senegal who had been exposed to fluoride drinking water levels of 7,4 mg/ℓ and 11mg/ℓ, 26% had developed crippling skeletal fluorosis. There were more cases of crippling skeletal fluorosis than those reported for the entire of the USA. The reason for this marked difference at essentially the same fluoride level is most likely due to marked differences in local conditions, such as diet, water consumption rates which could result in higher fluoride exposure.

Fluoride effects on bone tissues have been found to be cumulative and manifests in a number of stages with the less serious occurring early in the natural course of the disease. Whatever may be the type of fluoride exposure, the clinical picture in chronic poisoning occurs in the following phased manner.(Dean, 1942b)

Table 8: Phases of Skeletal fluorosis

Preclinical phase	Asymptomatic, slight radiographically detectable increases in bone mass.
Phase I	Musculoskeletal: sporadic pain, stiffness of joints, osteosclerosis of pelvis and spine.
Phase II	Degenerative and destructive: chronic joint, arthritic symptoms, slight calcification of ligaments, increased osteoclerosis.
Phase III	Crippling fluorosis: limitation of joint movement, calcification of ligaments/neck, spinal column, crippling deformities/spine and major joints, muscle wasting, neurological defects/compression of the spinal cord.

Whether dental or skeletal fluorosis is irreversible or not and if no treatment exists, the only remedy is prevention by keeping the fluoride intake within safe limits. In places where fluorosis is due to excessive intake of fluoride from drinking water, there should be a shift from that source of drinking water to alternative water sources with lower fluoride concentration or the water should be partially de-fluoridated. Since alternative water resources are scarcely available, especially in developing countries in Africa and Asia, the only solution is de-fluoridation. The constraint is that these methods have proved to be expensive. Prolonged exposure to 10-20 mg fluoride/person/day for more than six years can lead to crippling skeletal fluorosis, in which osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity result.

3.4.3.3 Other effects

Chronic effects on the kidneys have been observed in persons with renal disorders including effects on the thyroid gland, which may occur with long term-exposure to high fluoride concentrations (WRC, 2001). The data and documented information available on this subject are, however, too limited to allow a quantitative evaluation of the increased sensitivity to fluoride toxicity of such persons. (Janssen, *et al,* 1988).

Where incidents of acute intoxication have been reported following overdosing in water supplies, fluoride levels have ranged from 30 to 1000 mg/ℓ (Janssen, *et al*, 1988). Some acute effects at high fluoride concentrations include haemorrhagic gastro enteritis, acute nephritis and injury to the liver and heart muscle tissues. Many symptoms of acute fluoride toxicity are associated with the ability of fluoride to bind to calcium. However, the details of other fluoride effects in human beings are beyond the scope of this dissertation.

3.4.3.4 De-fluoridation techniques

As soon as excessive amounts of fluorides in water supplies had been established as the cause of dental fluorosis, research on methods of de-fluoridation were initiated. The passing of water through various types of de-fluoridation media such as tricalcium phosphate, bone char, fishbone charcoal, (Bhargava and Killedar, 1992), bone meal and activated alumina was found to accomplish fluoride removal by a combination of ion exchange and sorption. Fluorides can also be removed during lime softening through co precipitation with magnesium hydroxide, or by alum coagulation (Schoeman and Botha, 1985; Schoeman, 1987;Saha, 1993). The details of these methods are not discussed in this dissertation.

Concerns about the effects of fluorides on human health have led a lot of countries to be engaged in research work. This has included the determination of safe levels, standards and guidelines for fluoride ion concentrations in drinking water.

3.5 DRINKING WATER GUIDELINES AND STANDARDS FOR FLUORIDE

A lot of work has been done to establish drinking water standards for fluoride in South Africa and in other countries of the world. (Laksham, 1979; Hammer, 1986; Brouwer, *et al.*, 1988; WHO, 1996). The general conclusion emanating from all findings is that it is particularly important to consider climatic conditions, volumes of water intake and other factors in setting national standards for fluoride. This point is extremely important, not only in setting national standards for fluoride but also in taking data from one part of the world and applying it in regions where local conditions are significantly different.

Temperature has been used in most cases to determine the optimum fluoride concentration at which minimal or no health effects will occur. This is because of a general understanding that water consumption is dependent upon environmental temperature. (Laksham, 1979; Hammer, 1986 ; DWAF, 1996). In 1992, J. B. du Plessis in the OFS Goldfields in South Africa conducted a study. The aim of this study was to determine the maximum concentration of fluoride in water that will not cause dental fluorosis. When comparing the results of this study with the results from other studies in the USA an extrapolation of 0,7-mg/ℓ-fluoride concentration was made for the study area.

In South Africa, the Target Water Quality Range (TWQR) of 0-1,0 mg/ℓ fluoride is set for human health. This is the concentration range in water necessary to meet requirements for healthy tooth structure. This concentration is a function of daily water intake and hence varies with annual daily air temperature. A concentration of approximately 0,75 mg/ℓ corresponds to a maximum daily temperature of approximately 26^0C–28^0C. No adverse health effects or tooth damage is expected under these conditions. (DWAF, 1996). The following tables show the current guidelines, recommendations and standards for fluoride in South Africa. The guidelines are specifically for drinking water or domestic purposes. It should be noted however that the South African Water Quality Guidelines are aimed at protecting the water resources such that the water remains fit for its intended uses. They thus only give a description of the effects on water users when the concentration of a particular constituent increases beyond the recommended level.

Table 9: Drinking water quality standards and guidelines for fluoride in South Africa, effects of fluoride on aesthetics and human health

Fluoride Range (mg/ℓ)	**Effects**
Target Water Quality Range (0-1,0)	The concentration in water necessary to meet the requirements for healthy tooth structure is a function of daily water intake and hence varies with annual maximum daily air temperature. A concentration of approximately 0,75mg/ℓ corresponds to approximately 26 to 28°C. ***No adverse health effects or tooth damage occurs.***
1,0–1,5	Slight mottling of dental enamel may occur in sensitive individuals. No other health effects are expressed.
1,5–3,5	The threshold for marked dental mottling with associated tooth damage will probably be noticeable in most continuous users of the water. No other health effects occur.
3,5–4,0	Severe tooth damage especially to infants' temporary and permanent teeth; softening of the enamel and dentine will occur on continuous use of the water. ***Threshold for chronic effects of fluoride exposure,*** manifested as skeletal effects. Effects at this concentration are detected mainly by radiological examination, rather than overt.
4,0–6,0	Severe tooth damage especially to the temporary and permanent teeth of infants, softening of the enamel and dentine will occur on continuous use of water. Skeletal fluorosis occurs on long-term exposure.
6,0-8,0	Severe tooth damage especially to the temporary and permanent teeth of infants, softening of the enamel and dentine will occur on continuous use of water. **Pronounced Skeletal fluorosis occurs on long-term exposure.**
>8,00	Severe tooth damage as above. Crippling skeletal fluorosis is likely to appear on long- term exposure
>100	Threshold for onset acute fluoride poisoning marked by vomiting and diarrhea.
>2000	The lethal concentration of fluoride is approximately 2000mg/ℓ.

Source: DWAF, 1996 (1st issue), South African Water Quality Guidelines for Domestic Water Use

In 1998, the Department of Water Affair and Forestry, the Department of Health and the Water Research Commission in South Africa jointly published an assessment guideline. The guideline is currently and widely used to assess the quality of domestic water supplies. Table 10 provides the guidelines for fluoride in drinking water.

Table 10: Fluoride guideline (WRC, 1998)

Fluoride range, (mg/ℓ)	DRINKING (Health	(Aesthetic)	FOOD PREPARATION	BATHING	LAUNDRY
<0,7	No health effects	No effects	No effects	No effects	No effects
0,7-1,0	Insignificant health effects in sensitive groups and insignificant tooth staining	No effects	Insignificant health effects in sensitive groups	No effects	No effects
1,0-1,5	**Increasing effects in sensitive groups and tooth staining**	No effects	**Increasing effects In sensitive groups**	No effects	No effects
1,5-3,5	Possible health effects in all individuals and marked tooth staining	No effects	Possible health effects in all individuals	No effects	No effects
>3,5	Increasing risk of health effects and severe tooth staining	No effects	Increasing risk of health effects	No effects	No effects

Blue-Ideal   Green-Good   Yellow-Marginal   Red Poor

Purple- Completely unacceptable

Table 11: Recommended quality (health) guidelines for drinking water for elements and ions in the Republic of South Africa (RSA) waters, (DWAF, 1996). All values in mg/ℓ except pH and EC.

N.B parameters selected below are of interest to the fluoride chemistry in water

Parameter in mg/ℓ except for EC and pH	**Maximum limit of no risk, ideal-good**	**Low risk range, Marginal**	**Medium – high risk range, Poor-unacceptable**
EC (mS/m, 25°C)	150	150-370	370
pH low	4.5	4,5-4,0	< 4,0
pH High	10	10-10,5	>10,5
Ca	150	150-300	>300
Mg	100	100-200	>200
Na	200	200-400	>400
K	50	50-100	>100
Cl	200	200-400	>600
SO_4	400	400-600	>600
F	1,0	1,0-1,5	>1,5
$(NO_3 + NO_2)$ as N	10	10-20	>20

The guidelines presented in Tables 9, 10 and 11 above are currently in use in the country as they strongly complement each other. This assist both the user and water provider in assessing the quality of the water and taking appropriate decisions in cases where the water does not comply with set guidelines and limits.

Table 12: Chemical requirements-macro determinants for drinking water. Standards for drinking water.

1	2	3	4	5	6
Determinants	Units	Upper limit and ranges			Class II water consumption period, [a] max.
		Class 0 (Ideal)	Class 1 (Acceptable)	Class II Max.allowable	
Ammonia as N	mg/ℓ	<0,2	0,2-1.0	>1,0-2,0	No limit[b]
Calcium as Ca	mg/ℓ	<80	80-150	>150-300	7 years
Chloride as Cl^-	Mg/ℓ	<100	100-200	>200-600	7 years
Fluoride as F^-	mg/ℓ	<0,7	0,7-1,0	>1,0-1,5	1 year
Magnesium as Mg	mg/ℓ	<30	30-70	>70-100	7 years
(Nitrate and nitrite) as N	mg/ℓ	<6.0	6,0-10,0	>10,0-20,0	7 years
Potassium as K	mg/ℓ	<25	25-50	>50-100	7 years
Sodium as Na	mg/ℓ	<100	100-200	>200-400	7 years
Sulphate as SO_4^{2-}	mg/ℓ	<200	200-400	>400-600	7 years
Zinc as Zn	mg/ℓ	<3,0	3,0-5,0	>5,0-10,0	1 year

[a] The limits for the consumption of class II water are based on the consumption of 2ℓ of water per day by a person of mass 70kg over a period of 70 years.

[b] These values can indicate process efficiency and risks associated with pathogens.

Source: SABS 241*, Edition 5, 2001

3.6 Optimum fluoride levels

The optimum fluoride level in water is the level that produces the greatest protection against caries with the least risk of fluorosis. Based on fluoridation studies conducted in the United States, the US Environmental Protection Agency has established optimum and approval limits for fluoride in public water supplies. (Hammer,1986; WRC, 2001). Similar exercises have been accomplished in other parts of the world including Africa. The recommended optimum concentration for a community is based on the annual average of the maximum daily air temperature from temperature data obtained for a minimum of 5 years and is calculated as follows:

$$Copt = (0,34)/(0,16 + 0,11\ T)$$

Where Copt = optimum fluoride concentration, mg/ℓ

T = annual average maximum daily air temperature in ^{0}C.

The following formula has recently been used in South Africa for the calculation of optimal fluoride ion concentrations in drinking water.

$$\text{Optimal } F^{-} = [0,34] / [0,2364 + 9T/5*0,0062]$$ (WRC, 2001)

The approval limit, which is the maximum allowable concentration to prevent excessive dental fluorosis, is double the optimum concentration. The requirements of the Department of Health for health teeth are based on the optimum concentration to promote dental health.

CHAPTER 4 RESEARCH PROCEDURES

4.1 INTRODUCTION

For many years the Department of Water Affairs and Forestry has been gathering groundwater quality data from around the country as part of ad hoc groundwater resources investigations. Yet little national-scale investigation of data has taken place, except for the depicted map on the Groundwater resources of the Republic of South Africa (Vegter, 1995). This data gathering process intensified over the past years as a result of regional groundwater mapping programmes and the establishment of a national groundwater quality-monitoring network in 1994.This included the big survey that was done by the Chief Directorate Water Services of the DWAF on the quality of water used for domestic purposes throughout South Africa. This survey was based on existing data obtained from DWAF 's databases as well as data from other organisations and Non-governmental organisations (NGOs). The groundwater quality data collected prior to 1994 was transferred onto the National Water Quality Database (QUALDB). This database containing over 55 000 analyses of groundwater samples, mostly of macro elements, has been recently replaced by the Water Management System (WMS). At the time of writing this dissertation this transfer was ongoing. It is possible that some of the data, which will be a few points, were not yet on the WMS. Data from the National Groundwater Quality Monitoring Network is included.

4.1.1 Water Management System (WMS)

The Water Management System is housed at the Institute for Water Quality Studies (IWQS), a directorate within the Chief Directorate Scientific Services of the DWAF. It is a computer programme developed specifically for DWAF to support decision-making and provide the necessary information needed to manage water resources, sources and monitoring in South Africa. The system comprises of various core components, which include:

- Resource and source management
- Monitoring management
- Registration of samples and results
- Water network management
- Stakeholder list
- Extracting and reporting of results
- Web enablement

- Environmental Questionnaire
- Feature in management
- Compliance Manager
- Letter generation (DWAF, http://www-dwaf.pwv.gov.za/Projects)

4.1.2 The National Groundwater Quality Monitoring Project

The project started in 1994 with the monitoring of 376 sites to ascertain the influence of rainfall on groundwater quality and to determine the groundwater quality on a national scale. The monitoring points for the project are as shown in Fig 3 below. The monitoring points are being sampled twice a year, that is before and after the rainfall season (October and April respectively). The samples are usually analysed by the laboratories at the IWQS and the data is forwarded onto the WMS.

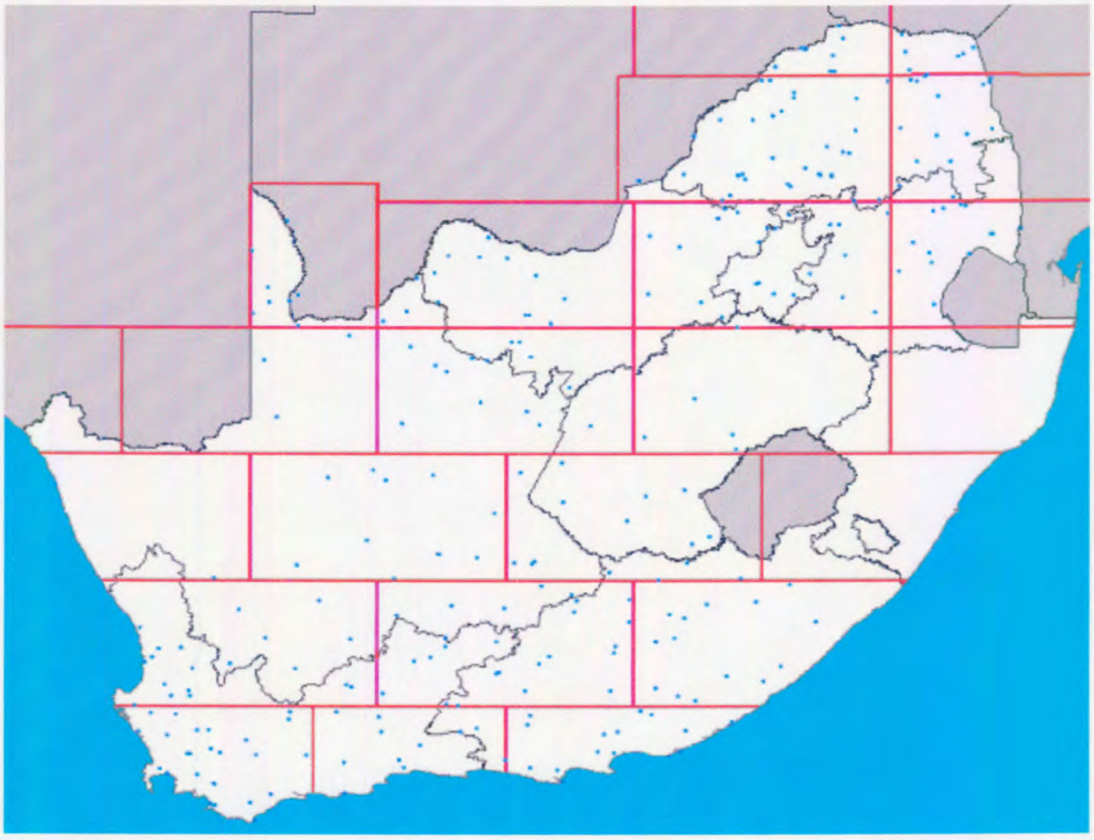


Fig 3: Locations of current groundwater quality monitoring points

4.2 THE DETERMINATION OF THE FLUORIDE ION CONCENTRATION DISTRIBUTION IN GROUNDWATER

Using the extraction and reporting core component of the WMS, 44 886 groundwater analyses for fluoride were extracted and downloaded from the database. The set of data was checked for obvious errors. These were eliminated. This resulted in a data set comprising of 36046-groundwater analyses for the fluoride ion concentration. This data set was used to determine the overall fluoride ion distribution in groundwater between 1985-2000 in South Africa. Areas with fluoride ion concentrations lower or higher than the recommended guidelines and standards for fluoride in drinking water were also delineated. The highest fluoride ion concentrations recorded in each primary drainage region during the study period was also identified. The analysis with a spatial component was done using a Geographical Information System (GIS) software package, ARC/INFO. Lithological boundaries were digitised from the 1:250000 scale geological map of South Africa. The SABS maximum standard limit of 1,5 mg/ℓ for fluoride in drinking water was adopted as one of the upper intervals for protection against dental fluorosis. Since fluoride levels in drinking water required to prevent tooth decay and dental fluorosis have been reported as ranging from 0,5 to 1,0 mg/ℓ (WHO, 1994; Du Plessis, 1995), the minimum beneficial limit used for this study is hence estimated at 0,5 mg/ℓ. The rest of the ranges were estimated on DWAF guidelines for drinking water (DWAF, 1996). The optimum range for good dental health, according to most guidelines and standards for drinking water (WHO, 1984; WHO, 1994; DWAF, 1996; SABS, 2001) is 0,7-1,0mg/ℓ F^-. These values have been used to represent the three beneficial intervals;

> 0,5 < = 0,7
> 0,7 < = 1,0
> 1,0 < = 1,5

Intervals in which dental health effects have been confirmed by research were used in plotting the data;

0 <= 0,5	effect of low fluoride ion concentration on dental health
>1,5 <= 4,0	Effect of excess fluoride
>4,0 <= 8,0	Effect of excess fluoride
>8,0	Effect of excess fluoride

The details of these guidelines and standards are tabulated in **Chapter Three**. The spatial distribution of the data was overlain on Vegter 's lithostratigraphy in order to assess the role of surface geology in the occurrence and distribution of fluoride in groundwater.

4.3 THE DETERMINATION OF THE CURRENT STATUS OF FLUORIDE LEVELS IN GROUNDWATER

4.3.1 Introduction

One of the important tools in Water Quality Assessment is the assessment of the current status or condition of the parameter or constituent of concern. This is usually a measure of the current condition (most recent 3-5 years) at a station or source compared to a benchmark value or data. In this study, the values for the fluoride ion concentrations between 1996 and 2000 were used to assess the current status of fluoride ion concentration levels in some national groundwater sources. The data set used was obtained from the data used **in section 4.2** above. The values in guidelines (DWAF, 1996; WRC, 1998) and standards (SABS, 2001) were used as a benchmark. The purpose of this was to determine the fitness for use of the groundwater for domestic use and as criteria to characterise the quality of water in the individual groundwater sources based on the fluoride ion concentration observed.

The data set was assessed using the comparison of the observed fluoride ion concentration values and those required for human health as indicated in the various standards and guidelines tabulated in Chapter 3 of this dissertation. The data set between 1996-2000 comprised of 14 509-fluoride samples, collected from the various groundwater sources. This included boreholes and springs. A statistical package, STATISTICA, which calculated a fluoride median value for each unique groundwater source was used to process the data. This resulted in a summarised data set comprising of 6042 values.

Two approaches were used in assessing the data. These were the frequency and spatial distribution. The data was plotted on maps to indicate the current distribution of fluoride ion concentration levels in South African groundwater sources and a histogram was constructed to indicate the frequency of the occurrence of these levels. The identified sources were characterised and classified accordingly.

The results from these exercises were compared with the dental fluorosis results and areas of concern identified. Some of these areas were physically labelled on the maps and linked to other results for better clarification of observations made especially those sources containing fluoride ion concentrations higher than the threshold for chronic poisoning. The use of such sources for drinking water purposes could lead to severe tooth damage and skeletal fluorosis.

Three adequately monitored boreholes were selected to study the interactions of the fluoride ion with other water quality parameters. Three of the boreholes were selected in the following order: good groundwater quality, and moderately higher fluoride concentrations than the recommended limits, and one having high fluoride ion concentrations. Correlation studies were carried out for these parameters. The main aim was to determine the role and contribution of parameters such as total alkalinity, silicates, phosphate, pH, Hardness (Mg+Ca), Na, and electrical conductivity (EC). Pearson product moment correlation, from STATISTICA was used for this study.

4.4 THE DETERMINATION OF TRENDS IN CHANGES OF FLUORIDE ION CONCENTRATIONS IN GROUNDWATER

The data points described in **4.3** above were processed further in order to select those sites, which were monitored regularly during the selected assessment period. It was observed that for some monitoring points, monitoring was done only in a single year or two. For others monitoring did not start until 1997. The remaining data set was found suitable for the performance of a short-term trend analysis but a provisional attempt indicated that it would not be feasible to carry out the exercise given the following reasons.

- Changes in groundwater quality parameters are generally slow given its nature and hence trends may not be apparent in the water quality data for several years.
- Many factors such as, groundwater contamination from different sources, seasonal cycles, precipitation and natural availability of fluoride might affect the measured and observed water quality. As a consequence, it often takes many years of regular water quality data collection to statistically detect a trend, which usually manifests in small, gradual changes. Ultimately, if ever a trend is identified, additional scientific assessment is often essential to understand the implications of the trends and identify corrective actions.

4.5 DENTAL EXAMINATIONS

An independent data set was necessary for this study. This was used to determine the impact of consuming or drinking water with high fluoride ion concentrations levels on dental health. The areas of potential risk could be estimated from the various maps. For this reason the results from the assessment of this data set were compared with the water quality results in terms of fluoride ion concentration levels. At the time of writing this dissertation, the National Department of Health (NDOH) conducted a national survey on dental fluorosis. School children were examined in all the nine provinces of the country. Representatives from the Department of Health did the examinations. Symptoms of chronic dental fluorosis or mottled teeth were also looked for during the dental examinations. Detailed particulars about the degree of mottling, as well as the area where these children were born and had lived in up to the age of 12 years were carefully recorded. All cases of mottling were classified according to Dean, 1939 (Table 12 below). The data for this survey is currently housed at Statistics South Africa (SSA). Access to the data is arranged through the Department of Health. The data received from the Department of Health was plotted after calculating total dental fluorosis morbidity for each area. The method for calculating the total % morbidity of dental fluorosis was adopted from Wang, *et al* 1999. A comparison of the results obtained from the occurrence of the fluoride ion concentrations in groundwater and the incidences of dental fluorosis in selected provinces was done.

Table 13: Description and rating of dental fluorosis, according to Dean, 1939

Degree of fluorosis	Description and rating
Normal	**0**
Questionable	**0,5** A few white flecks to occasional white spots
Very Mild	**1,0** Less than 25% of the tooth 's surfaces covered by white opaque, paper-white areas.
Mild	**2,0** Fifty percent of the tooth 's surfaces covered by White opaque areas.
Moderate	**3,0** nearly all the tooth 's surfaces involved in minute pitting and brown staining.
Severe	**4,0** Smoky white appearance of all the teeth Pitting frequent and on all tooth 's surfaces Hypoplasia, chipping and large brown stains that vary from chocolate brown to black.

4.6 COMPUTER MANIPULATION OF SPATIAL DATA

Analysis of data with a spatial component was carried out using the Geographical Information System (GIS) software package ARC/INFO. Lithological boundaries were obtained from the maps produced by Vegter (Vegter, 1995). In order to classify groundwater data in terms of surface geology, various geology maps were used. This was the most accurate and available method for performing the classification since a large number of data points were used. To produce various maps the fluoride ion concentrations in groundwater samples were classified into 7 groups: 0-0,5; 0,5-0,7; 0,7-1,0; 1,0-1,5; 1,5-4,0; 4,0-8,0 and >8.

4.7 THE ANALYTICAL METHOD USED FOR FLUORIDE ANALYSIS

The fluoride ion-selective electrode method was used to measure fluoride ion concentration in solution. The use of the Total Ionic Strength Adjustment Buffer (TISAB) brings all solutions approximately to the same ionic strength and to a pH of approximately 5,5. It is also intended to break up aluminium fluoride and related complexes that might otherwise reduce the fluoride activity (Hammer, 1986). Cyclohexene diamine tetraacetic acid (CDTA) is used as an effective de-complexing agent.

CHAPTER 5 RESULTS AND DISCUSSION

5.1 INTRODUCTION

In this chapter the results obtained using the research procedures described in Chapter 4 are presented and discussed in the following sections:

- Occurrence and distribution of fluoride ion concentrations in groundwater; 1985-2000
- The highest fluoride ion concentrations recorded in South Africa between 1985-2000;
- The status of fluoride ion concentration levels in South African groundwater, 1996-2000
- The occurrence of dental fluorosis in selected provinces and
- The distribution of percentage morbidity of dental fluorosis in selected provinces
- Dental fluorosis and drinking water quality
- Factors that contribute to the occurrence of different fluoride ion concentration levels in groundwater **(as identified in this study)**;

5.2 OCCURRENCE AND DISTRIBUTION OF THE FLUORIDE ION CONCENTRATION IN GROUNDWATER, 1985-2000

5.2.1 Spatial distribution of fluoride ion concentrations in groundwater

The overall picture on the distribution of fluoride ion concentrations in groundwater and the potential exposure to fluoride that may exist from those groundwater sources is shown in Map A. Maps A1-A3 show the distribution of those sources with the fluoride ion concentrations beyond the safe recommended limits for drinking water. Map A4 shows the distribution of sources with fluoride ion concentrations between 0 and 0,5 mg/ℓ. Such areas are generally considered as deficient in fluoride where these levels persist for a long time. If such a situation persists, then the people using the water for drinking purposes will be susceptible to dental caries problems and they might be a need for fluoride supplementation in the form of fluoridation.

However caution must be exercised as the same sources might exhibit higher concentrations at any time given the climatic conditions, type of aquifer, and type of geology among other factors. The values given in this document do not necessarily reflect the actual values that may exist at all times in a given groundwater source, nor do they reflect the actual or constant exposure to fluoride of the population of South Africa although in exceptional cases that can be true.

In all the maps a comparison of the fluoride levels and their distribution compared to the SABS standards for drinking water and DWAF guidelines as described in Chapter 3 was made. The data is plotted on the geology map to allow for a comparison between the occurrence of the fluorides and the surface geology. It is envisaged that this comparison would give an insight into the role of geology in the occurrence of fluoride ion concentration levels in groundwater. Seven intervals commensurate with the guidelines and drinking water standards were selected for plotting the data. The maps are separated to facilitate the delineation of those areas deficient in fluoride and those with high potential for dental fluorosis. (Maps A1-A4). The maximum allowable limit for fluoride ion concentration in drinking water is 1,5 mg/ℓ. According to the SABS, this water can be consumed for a maximum period of one year in order to avoid the occurrence of dental fluorosis. Map A1 shows the distribution of sites with fluoride ion concentration of 1,5-4,0 mg/ℓ. It should be noted that prolonged consumption of this water could result in severe dental fluorosis or skeletal fluorosis in some instances.

From the maps, it is evident that groundwater is generally of good quality but certain areas experience problems of high fluoride ion concentrations. Maps A and A4 support this. A number of cases with higher fluoride ion concentrations in groundwater than the recommended limits for drinking water occur in the Limpopo, Northern Cape, Eastern Cape, KwaZulu Natal and North-West provinces. The Northern Cape is the most affected province. This is evident from Maps A1-A3. Of more concern are those cases with fluoride ion concentrations greater than 8mg/ℓ. The Limpopo, Northern Cape, KwaZulu Natal and Eastern Cape provinces have a number of such cases (Map A3). In other provinces a few cases or individual sources are observed. These include Mpumalanga and Free State. The consumption of these levels of fluoride can lead to serious health problems. Most of these areas have been found to be endemic to fluorosis. (Map C, C1 and C2).

It is evident from the maps that most of the groundwater sources have fluoride concentrations above the maximum limit of 1,5 mg/ℓ recommended by SABS and DWAF for drinking water. Of more concern is the number of boreholes with concentrations above **the threshold for chronic fluoride poisoning**, which might lead to severe dental fluorosis and crippling skeletal fluorosis. (Maps A2 and A3).

In conclusion, the results show a country in which in most provinces groundwater sources have fluoride ion concentrations higher than those recommended for fluoride in drinking water. If the results shown in Map A4 are considered a true reflection of the fluoride levels in drinking water actually consumed by the population then no area is in need of fluoridation to within 0,5-1,0 mg/ℓ as recommended by the World Health Organisation (WHO, 1994) or 0,7-1,0 mg/ℓ (DWAF, 1996, SABS, 2001). If the local people are using all the examined sites for drinking purposes, then a large number of the groundwater sources of South Africa are in need of partial de-fluoridation. This will be true for most of the groundwater sources in the Limpopo, North-West, Northern Cape, Western Cape and KwaZulu Natal Provinces.

Map A4 delineates those areas with fluoride ion concentrations lower than the recommended limits for dental health, <0,5 mg/ℓ (WHO, 1994). However, this water is considered ideal according to the South African Water Quality Guidelines (DWAF, 1996, WRC, 1998) since the concentrations are <0,7 mg/ℓ. This sets a contradiction between the requirements as set by the Department of Health for the fluoridation of water supplies once the fluoride ion concentration is <0,7 mg/ℓ and the DWAF guideline for fluoride. The DWAF's TWQR for fluoride in drinking water, which is the concentration in water necessary to meet the requirements for health tooth structure as a function of daily water intake and varying with annual daily air temperature is between 0-1,0 mg/ℓ. According to the guidelines the consumption of this water will have no health effects. This water is classified as Class 0 and ideal for drinking according to the SABS specifications (SABS, 2001). Given these conditions and the pattern of distribution of these concentration levels observed in Map A4, it will be safe to conclude that groundwater is generally of good quality.

It should however be noted that if a population is subjected to very low fluoride ion concentrations, dental caries might be a problem. Considering, the fact that fluoride levels vary from time to time given the factors that contribute to its occurrence in a locality, it would be a risk to recommend that there be fluoridation across the country or for specific boreholes. A rather safe means will be to find other means of supplementing fluoride such as fluoride tablets to children or administer fluoridated toothpaste.

5.2.2 The highest fluoride ion concentrations recorded in South Africa between 1985- 2000

The highest fluoride ion concentrations recorded for the various sites across the country and in the individual primary drainage regions are given in Table 14 below. The fluoride ion concentrations ranged between 2,75 and 42,05mg/ℓ.

Table 14: Highest fluoride ion concentrations recorded for the State and Individual Primary Drainage Regions(PDRs) as reflected by the WMS data (1985-2000)

PDR	No. Of analyses	Place	F ion concentration, Year recorded
All	36046	Elandsfontein 321	42,05 (1994)
A	7409	Zoutpan, North West	40,77(1995)
B	3115	Doornkloof, Eastern Cape	39,63 (1988)
C	6737	Rissiville, Gauteng	38,3 (1985)
D	7427	Marlborough, Northern Cape	34,64(1995)
R	993	Richmond Hill, Eastern Cape	2,75 (1990)
F	564	Bitterfontein, Western Cape	10,37 (1997)
G	2183	Mitchellsplein, Western Cape	14,78(1998)
H	284	Pietersfontein, Western Cape	10,71 (1997)
J	840	Fonteintjies, Western Cape	15,93 (1989)
K	188	Farm 138, Western Cape	6,98 (1990)
L	620	Doornkloof, Eastern Cape	39,63 (1988)
M	499	The Apex, Eastern Cape	3,92 (1990)
N	968	Grasrand, Eastern Cape	19,52 (1988)
P	332	Dagbreek, Eastern Cape	10,28 (1990)
Q	457	Klippe Drift, Eastern Cape	16,83 (1985)
S	124	Kumngqanga, Eastern Cape	6,21 (1990)
T	283	Roodeberg, KwaZulu Natal	12,3 (1997)
U	172	KwaZulu, KwaZulu Natal	7,14 (1991)
V	421	Golokodo, KwaZulu Natal	15,72 (1992)
W	1357	Machibini, KwaZulu Natal	23,56 (1992)
X	958	Kasteel, Limpopo	40,49 (1994)

From the above, it is observed that cases of high fluoride ion concentration in groundwater occur in almost all provinces and primary drainage regions although some are more affected than others.

5.3 THE STATUS OF FLUORIDE LEVELS IN GROUNDWATER AS REFLECTED BY GROUNDWATER SOURCES STUDIED BETWEEN 1996-2000

In order to study the status of fluoride concentrations in various groundwater sources across the country between 1996-2000, two approaches were used namely spatial distribution using ARC/INFO, a GIS software and the frequency distribution. The 6042 data points extracted from the WMS for the period 1996-2000 were plotted as shown in Map B **(details in Chapter 4)**. To simplify the interpretation of the results observed and account for the various levels of fluoride in groundwater, the data was plotted on Vegter's lithostratigraphy (Vegter, 1993). This allows the assessment of the effect of surface geology in the occurrence and distribution of fluorides.

5.3.1 Spatial distribution

The current status of fluoride ion distribution in South African groundwater is shown in map B. The map shows that the problems of high fluoride ion concentrations are currently being experienced in the Limpopo and Northern Cape provinces. A few cases were recorded in other parts of the country. Other provinces experience the problem in a limited number of groundwater sources. It should be noted however that all levels and ranges of fluoride occur to a certain degree in almost all provinces. The Map B1 shows a comparison between the distribution of fluoride using the data from the current study and that done by Simonic in 2001 (Simonic, 2001).

It is evident from the two maps that although groundwater is general of good quality there are serious problems of high fluoride levels, > 1,5 occurring in the groundwater sources of the Limpopo, North-West and the Northern Cape provinces. In other provinces such cases are observed as isolated incidents. The current situation of the fluoride distribution in the country is such that no clear cut demarcation can be made of the areas deficient in fluoride since some of those areas have sources in which the fluoride ion concentration is higher than the recommended limits for drinking water. Many groundwater sources in the Limpopo, North-West, Northern Cape, Western Cape and KwaZulu Natal provinces show a need for partial de-fluoridation. This must receive serious consideration if the water from those sources is currently being used for drinking purposes.

5.3.2 Frequency Analysis

The distribution of the fluoride ion concentrations calculated for the 6042 stations are shown in a bar chart. (Fig 4). From the chart it is evident that the population is highly skewed towards high fluoride concentrations. Although the tail of the graph is irregular, there is an increased frequency of occurrence of groundwater sources with fluoride ion concentrations in the range > 1,5-4,0 mg/ℓ. This is of concern, as the health impacts on teeth can become a problem at these levels.

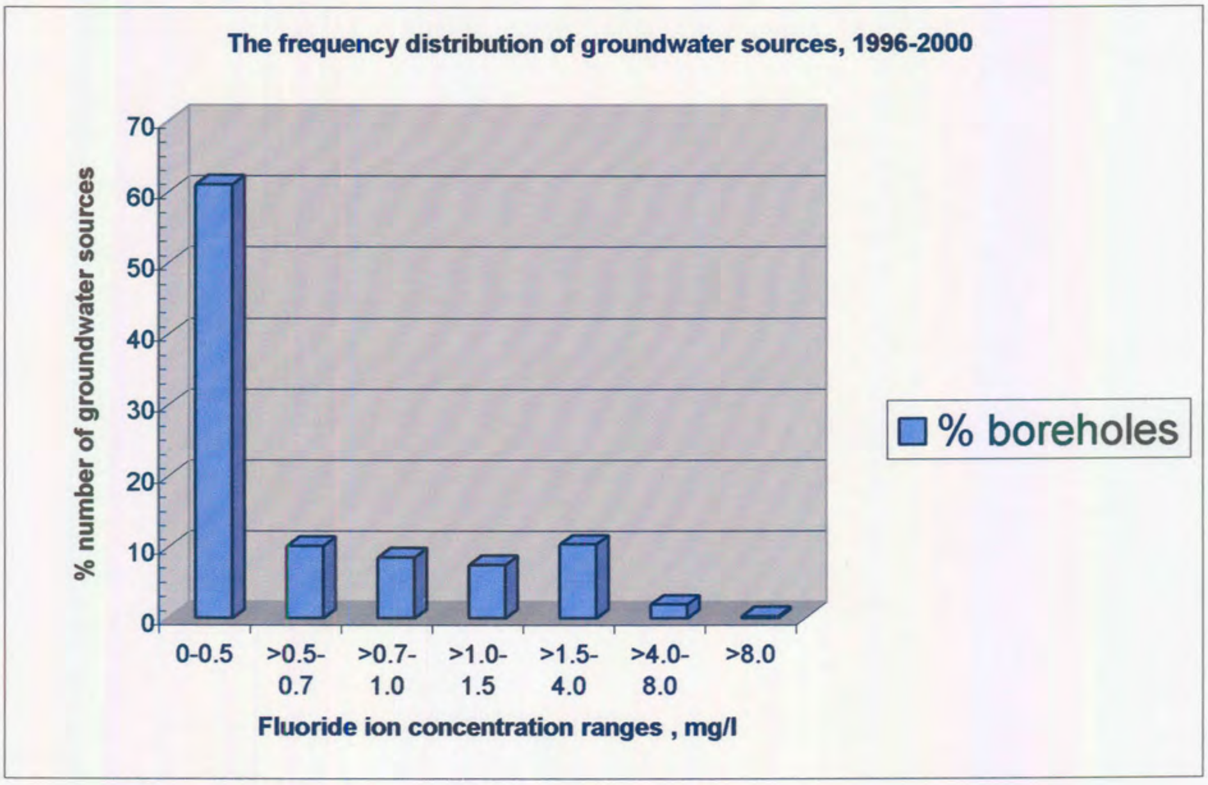


Fig 4: The distribution of fluoride ion concentrations for the groundwater sources, 1996-2000.

Of the 6042 groundwater sources studied;

3693 (61,1%) had fluoride ion concentrations less or equal to 0,5 mg/ℓ.

622 (10,2%) had fluoride ion concentrations between 0,5-0,7 mg/ℓ.

This brings to 4315 (71,3%) groundwater sources with concentrations of fluoride < 0, 7 mg/ℓ.

This is the current ideal standard according to SABS specifications selected based on the threshold for dental caries risk. Of all the groundwater sources assessed, 74,86% were within the TWQR of 0-1,0mg/ℓ F recommended by the DWAF for drinking water (DWAF, 1996). It can be concluded that generally, the water in South African groundwater sources is of good quality. From the 6042 groundwater sources studied, 456 (7,5%) had fluoride ion concentrations higher than 1,0 mg/ℓ but less than 1,5 mg/ℓ placing the water from these sources in the Class II category as recommended by SABS. The people drinking this water can only use it for a maximum period of one year. At this level, slight mottling of teeth may occur in sensitive individuals (DWAF, 1996; WRC, 1998). Currently this is the maximum allowable limit for fluoride in drinking water.

From the histogram it can be observed that there is an increase in the number of sources with fluoride ion concentration levels higher than 1,5 mg/ℓ but equal or less than 4,0 mg/ℓ. This is within the threshold limit for chronic effects of fluoride exposure. Both dental fluorosis and skeletal fluorosis may be detected if the water is consumed for a long period since childhood. Only 117 groundwater sources had fluoride ion concentrations between 4,0 and 8,0 mg/ℓ. Exposure to this water for drinking purposes will cause severe tooth damage and pronounced skeletal fluorosis if the candidates are exposure is for a long time (DWAF, 1996). Crippling skeletal fluorosis is also likely to appear. Of the studied groundwater sources, 19 (0,30%) had fluoride ion concentrations higher than 8,0 mg/ℓ. It should be noted however that it is not the quantity of the groundwater sources that is important but the level of fluoride ion concentrations of the water, the impact on health and the population at risk due to the consumption of such water.

It should be noted that there is a contradiction in what is understood as the safe limit for fluoride in drinking water. While the SABS, the DWAF and WHO agree on the safe limit of < 0,7 mg/ℓ for the fluoride ion concentration as ideal for health teeth, the DOH legislation enforces that the fluoride ion concentration should be equal to 0,7 mg/ℓ. According to the WHO a concentration of 0,5 mg/l is ideal for dental health (WHO, 1994) hence concentrations <0,5mg/ℓ might cause dental caries if the water is consumed for a long time.

Fluoride ion concentrations < 0,5mg/ℓ fall within the safe and ideal range according to the SABS and the DWAF while at these levels the DOH recommends the fluoridation of water supplies. Considering the fact that the majority of the population does not yet have access to piped water and it is difficult to fluoridate borehole water, water from natural springs and wells, it will be appropriate to recommend that alternative methods of fluoridation such as fluoridated vitamins and minerals, fluoride tablets, fluoridated salt, fluoride-containing mouth rinses and fluoride containing toothpaste. Professional supervision and public awareness campaigns need to accompany this. Research into these alternative methods need also to be carried out.

5.4 THE OCCURRENCE OF DENTAL FLUOROSIS IN SELECTED PROVINCES

The results of the general investigations of fluorosis obtained by analyzing the data from the DOH are as presented in Tables 16, 17, 18 and 19. The criteria used to interpret the results are as presented in Table 15. adopted from Wang, *et al.*, 1999. The information on the dependency of communities on groundwater for use as drinking water is presented in Table 20. This information was obtained in order to confirm the link between high fluoride levels in groundwater, the consumption of this fluoride contaminated water and the occurrence of dental fluorosis in the same areas. It should be noted that in a province where the communities depend largely on groundwater for drinking water purposes like the North-West Province, the morbidity of dental fluorosis is high.

Table 15: Criteria used for the interpretation of Dental fluorosis results. % Morbidity = (B + C)

Class	Dental Fluorosis symptoms
A-Normal	No apparent abnormality
B-Slight (Questionable, Very mild, Mild)	Yellowish teeth with slight erosion
C-Heavy (Moderate and Severe)	Extended erosion or mottling or heavy damage to teeth.

Table 16:Dental Fluorosis by level of Severity in the Free State (FS) Province
(Age group 12)

Name of Place	Class A	Class B	Class C	B + C	% Morbidity
FS-Region A	34.5%	62.2%	2.5%	64.7%	64.70
FS-Region B	35.6%	62.3%	1.3%	63.6%	63.60
FS-Region C	66.1%	29.1%	3.0%	32.1%	32.10
FS-Region D	66.1%	31.5%	1.7%	33.2%	33.20
FS-Region E	66.5%	29.7%	1.7%	31.4%	31.40
FS-Region F	42.4%	51.4%	4.8%	56.2%	56.20

Table 17:Dental Fluorosis by level of Severity in the Western Cape (WC) Province (Age group 12)

Name of Place	Class A	Class B	Class C	B + C	%Morbidity
WC-Boland –Overberg Region	86.0%	13.3%	0%	13.3%	13.30
WC- Metro	54.5%	42.1%	2.2%	44.3%	44.30
WC- South Cape -Karoo	46.5%	39.2%	10.7%	48.7%	48.70
WC-West-Coast	69.4%	26.5%	1.4%	27.9%	27.90

Table 18: Dental Fluorosis by level of Severity in the North-West (NW) Province

(Age group 12)

Name of Place	Class A	Class B	Class C	B + C	%Morbidity
NW-Brits	32.8%	61.7%	5.6%	67.3%	67.30
NW-Delareyville	80.7%	5.8%	0%	5.8%	5.80
NW-Mafikeng	97.7%	0.9%	0%	0.9%	0.90
NW-Mogwase	6.7%	93.4%%	0%	93.4%	93.40
NW-Moretele	25.6%	35.3%	39.1%	74.4%	74.40
NW-Potchefstroom	82.8%	17.2%	0%	17.2%	17.20
NW-Rustenburg	81.9%	5.8%	0%	5.8%	5.80
NW-Ganyesa	26.7%	54.9%	18.4%	73.3%	73.30
NW-Klerksdorp	82.7%	13.5%	1.8%	15.3%	15.30
NW-Kuruman	42.3%	57.7%	0%	57.7%	57.70
NW-Lichtenburg	86.6%	12.8%	0.5%	13.3%	13.30
NW-Schweizer	71.7%	26.6%	1.6%	28.2%	28.20
NW-Taung	31.6%	60.7%	7.1%	67.8%	67.80
NW-Ventersdorp	73.3%	20%	6.7%	26.7%	26.70
NW-Vryburg	49.7%	43.6%	6.7%	50.3%	50.30
NW-Zeerust	47.8%	48.6%	2.1%	50.7%	50.70
NW-Wolmaranstad	61.1%	33.4%	5.6%	39%	39.00

Table 19: Dental Fluorosis by level of Severity in the KwaZulu Natal (KZN) Province (Age group 12)

Name of Place	Class A	Class B	Class C	B + C	%Morbidity
Durban	79.6%	10.9%	1.4%	12.3%	12.30
Jozini	50.7%	34.7%	2.5%	37.2%	37.20
Ladysmith	41.7%	50.8%	7.0%	57.8%	57.80
Newcastle	86.4%	7.6%	3.3%	10.9%	10.90
Pietermaritzburg	72.2%	23.1%	2.1%	25.2%	25.20
Port Shepstone	77.1%	17.5%	1.8%	19.3%	19.30
Ulundi	57.8%	38.2%	1.9%	40.10%	40.10

Table 20: Dependency of communities on groundwater for domestic purposes as provided by the DWAF 's Water Services Directorate.

Province	North-West		**Free State**		**KwaZulu Natal**	
Source	Communities	People	Communities	People	Communities	People
Groundwater	1063	1 411 707	72	122 161	807	2 416 721
Surface Water	221	2 099 461	149	3097 252	75	212 698
Combined Source	13	108 593	30	139 452	48	149 685
None	-	-				
Unknown	-	-			1563	5 624 304
Total	1297	3 619 761	251	3340 865	2493	8 403 408
Supply Potential						
Poor	160	48 733	-	-	-	-
Low	207	330 061	24	83 380	-	-
Moderate	341	1 220 101	99	905 112	996	2 590 125
High	266	1 620 011	124	2271 450	558	1 529 404
Very High	323	400 855	4	80 923	939	4 283 879
Total communities	**1297**	3 619 761	**251**	3340 865	**2493**	8 403 408
Total population		**3 619 761**		**3340 865**		**8 403 408**

5.4.1 Morbidity of dental fluorosis and drinking water quality

The distribution of dental fluorosis in selected provinces is shown in Maps C, C1, C2 and C3. Map C is based on the data from tables 17, 18 and 19. The maps C1, C2 and C3 show the spatial distribution of the current % dental morbidity of fluorosis morbidity for the Western Cape, North-West and KwaZulu Natal provinces. The fluoride data is overlain on each provincial map in order to correlate the level of the morbidity of dental fluorosis and fluoride levels in drinking water. It should be noted that there exist differences in the morbidity of fluorosis among the investigated provinces. It was difficult to present the Free State province data using the same format as the dental fluorosis data was reported in regions whose digital data was not present at the time of writing this dissertation.

From the results, a percentage morbidity of dental fluorosis as high as 97% was recorded in the North-West province. In comparing the distribution of the % morbidity of fluorosis with that of fluoride concentration in groundwater sources (C1 to C3), it is apparent that high morbidity of fluorosis has happened in areas where fluoride concentrations are extremely high and in most cases exceeding the limits for drinking water. In towns and villages where the water quality problem in terms of fluoride ion concentration is less serious, the morbidity of fluorosis is comparatively low. It is evident from the maps that the occurrence of dental fluorosis and its morbidity correspond to the levels of fluoride ion concentrations in drinking water. The size of the shaded part (% morbidity of dental fluorosis) in each area gives the idea of the general quality of drinking water consumed by the examined subjects. The following tables show a comparison of worst-case fluoride ion concentrations and the percentage morbidity of dental fluorosis recorded in each province.

5.4.1.1 North-West province

Table 21: Incidences of fluoride ion concentrations in groundwater sources of the North-West province and the percentage morbidity of dental fluorosis

Area	Worst case F^- conc, mg/ℓ *(This study)	Worst Case F^- conc, mg/ℓ Rawhani, 1986	Percentage morbidity of dental fluorosis
Vryburg 1	>8,0	-	46
Ganyesa	>8,0	25,8	73,3
Kudumane	>1,0	-	60,0
Mogwase	> 8,0	-	93,4
Vryburg 2	> 8,0	-	50,3
Taung	> 0,5	1,1	67,8
Schweizer Reneke	> 4,0	-	28,2
Delareyville	> 4,0	-	5,80
Wolmaransstad	> 1,0	-	39,0
Klerksdorp	> 0,7	-	15,30
Litchtenburg	> 1,0	-	13,3
Ventersdorp	> 1,0	-	26,7
Potchefstroom	> 1,0	-	17,2
Marico	> 4,0	-	50,0
Rustenburg	< 0,5	-	5,80
Mankwe	> 4,0	8,8	~ 98,0
Bafokeng	< 1,5	-	~ 6,0
Brits	> 4,0	-	67,3
Moretele 1	> 8,0	9,0	74,40

From the above table it is evident that low fluoride ion concentrations in drinking water result in low levels of morbidity of dental fluorosis while higher concentrations correspond with high percentage morbidity of dental fluorosis. It can be concluded therefore that the effect of fluoride on dental health depends on daily intake of fluoride and drinking water is the main source. Another conclusion from this study is that in most cases severe dental fluorosis did not occur unless the fluoride ion concentration in the groundwater sources was in excess of 1,0 mg/ℓ and the degree and severity of mottling increased as the fluoride level increased. It should however be noted that the consumption of dietary fluoride and hence the amount of fluoride consumed will depend on the climate of a place. For example, in hot climate the rate of water consumption per day is higher than during winter days. This is because of the temperature dependence of the daily water consumption. In South Africa, the recommended limit of < 0,7 mg/ℓ and a maximum allowable limit of 1,5 mg/ℓ is enforced.

As seen from the above table high fluoride sources are scattered and widely spread across the province. Of great concern are those areas with fluoride ion concentrations higher than 8 mg/ℓ especially in Ganyesa. In 1986, it was confirmed that in this area, alternative sources to use of groundwater were not easily found (Rawhani, 1986). Although the subject of low fluoride ion concentrations was touched in this study, no field investigations on dental caries were conducted. Since the results show no particular areas of concern, fluoridation of water sources might not be a priority for the country at the moment. However it can be recommended that for those areas that are confirmed to be deficient in fluoride, fluoridation studies be carried out on a pilot scale. Since the impact is only visible after a long time and is irreversible proper consultation with the affected parties should be made to accommodate and avoid problems at all levels.

It is evident from Map B that the coverage of water quality data from other areas is poor. It is possible that after the publishing of the research results conducted in the former Bophuthatswana, the use of affected boreholes were discontinued (Rawhani, 1986; Pelpoa, *et al.*, 1992; McCaffrey, 1993). The other possibility would be that the data is still in the hands of individuals and it was not passed onto the DWAF databases.

However, it can be concluded from the results of the current study that the occurrence of high fluoride ion concentrations in groundwater used for drinking purposes is accompanied by a high percentage morbidity of dental fluorosis. This varies from district to district and village to village. This was also observed for other provinces (Tables 22 and 23)

5.4.1.2 Western Cape province

Table 22: Incidences of fluoride ion concentrations in groundwater sources of the Western Cape province and the percentage morbidity of dental fluorosis.

Area	Worst Case (F conc in mg/ℓl) (This study)	% morbidity of dental fluorosis
Western Cape District 1(Boland – Overberg Region)	>8	13,30
Western Cape Metro District 2	>8	44,90
Western Cape District 6	>8	48,70
Western Cape District 5	>1,5<= 4,0	27,90

In the Western Cape Metro there are a number of groundwater sources with the fluoride ion concentration between 1,5 and 4,0 mg/ℓ. Only one source had a concentration >8 mg/ℓ. However, the fact that the majority of sources have the concentrations between 1,5 and 4,0 is already a concern since in this range dental fluorosis becomes a problem. The same was observed and could be concluded about District 6.

5.4.1.3 KwaZulu Natal province

Table 23: Incidences of fluoride ion concentrations in groundwater sources of the KwaZulu Natal province and the percentage morbidity of dental fluorosis.

Area	Worst Case (F conc in mg/ℓ) (This study)	% morbidity of dental fluorosis
Jozini	<4,0	37,20
New Castle	<1,5	10,90
Ladysmith	>8	57,80
Ulundi	>8,0	40,10
Pietermaritzburg	<0,5	25,20
Durban	<1,5	12,30
Port Shepstone	<=4,0	19,30

From Map C, it is evident that the occurrence of high fluoride levels in some groundwater sources is a problem in the provinces studied but the degree of severity and the impact on dental health varies from province to province, district to district and village to village.

5.4.2 Distribution of potential risk areas

Maps C1-C3 were used for this exercise. Only areas for which dental fluorosis data was available during the time of this dissertation were used. These included KwaZulu Natal, North-West, Free State and Western Cape Provinces. The maps show the level of dental fluorosis risk based on the percentage morbidity of dental fluorosis. Based on the DWAF and SABS guidelines and standards for drinking water, it has been decided in this study to classify the degrees of dental fluorosis risk as follows:

<0.7mg/ℓ - No risk

0.7 - 1.5 mg/ℓ - Low risk

>1.5 - 3.5 mg/ℓ- Medium risk

>3.5mg/ℓ High risk

The above classification resulted in the following tabulated information;

Table 24: Relationship between %dental fluorosis morbidity and drinking water fluoride levels in KwaZulu Natal province.

AREA	F conc range, mg/ℓ	%Dental fluorosis	Classification of risk
Durban	1,0-1,5	12,30	Low risk
Jozini	1,5-4,0	37,20	High risk
Ladysmith	1,5-4,0	57,80	High risk
Newcastle	0,7-1,5	10,90	Low risk
Pietermaritzburg	1,0-1,5	25,20	Low risk
Ulundi	1,0-1,5	19,30	Low risk
Port Shepstone	1,0-4,0	40,10	High risk

Table 25: Relationship between %dental fluorosis morbidity and drinking water fluoride levels in the North-West province.

Area	%dental fluorosis	F range, mg/ℓ	Main source for drinking water
Brits	67,30	0,00-9,86	No risk to High risk
Delareyville	5,80	0,66-1,22	Low risk
Mafikeng	0,90	0.7-1,0	Low risk
Mogwase	93,40	>8,0	High risk
Moretele	74,40	>8,0	High risk
Potchefstroom	17,20	1,0-1,5	Low risk
Rustenburg	5,80	0,47	No risk
Ganyesa	73,30	>8,0	High risk
Klerksdorp	15,30	1,0-1,5	Low risk
Kuruman	57,70	1,0-8,0	High risk
Lichtenburg	13,30	1,0-1,5	Low risk
Schweizer	28,20	1,5-4,0	Medium to High risk
Taung	67,80	4,0-8,0	High risk
Ventersdorp	26,7	>1,5	Medium risk
Vryburg	50,30	4,0-8,0	High risk
Zeerust	50,70	4,59-9,69	High risk
Wolmaranstad	39,0	1,5-4,0	Medium to High risk

From the above observations it can be concluded that the degree of mottling (dental fluorosis) depends on the amount of fluoride ingested. Although this is observed from the results accurate correlation of the degree of mottling of the teeth with the amount of fluoride in the drinking water in South Africa is difficult owing to variations of fluoride levels in groundwater and the dependency of this phenomena on the various factors which include among others the effect of climate. The other factor, which might contribute to the above results, is the injection of fluorides into the hydrological cycle through various industrial activities. Socio-economic factors need also to be considered as a lot of people move from the rural areas into urban areas in search for jobs.

5.4.3 Risk levels and optimum fluoride concentrations in drinking water

The Optimum fluoride content of drinking water means a fluoride concentration of not more than 0.7 mg/ℓ in a public water supply (Anon. 1998). It is however known that the optimum fluoride dosage is dependent on the annual average maximum daily air temperature (Hammer, 1986, Grobler and Dreyer, 1988). There is uncertainty as to the precise concentration of F^- in drinking water that is optimal for human health, as these will vary from country to country. Table 25 below, shows that the fluoride ion concentration limits for drinking water suggested by various international bodies vary considerably. It is apparent that the upper limit for avoiding widespread dental fluorosis is approximately 2,0 mg/ℓ, although this value is lowered in tropical climates because of increased water ingestion. Fluoride ion concentration calculated for South Africa using the data obtained from the South African Weather Bureau is presented in Appendix C. The optimum fluoride content from this study was approximately 0,8 mg/ℓ. It has been noted that since water ingestion is proportional to air temperature, the optimal F^- concentration in groundwater used for drinking purposes should be dependant on the mean maximum temperatures experienced in any area, (WRC, 2001). The empirical equation for optimal F^- concentration calculations is as shown in **Chapter 3.**

Table 26: Maximum fluoride ion concentration limits recommended for drinking water

BODY/ORGANIZATION	Proposed effects, mg/l F in drinking water		
	Objectionable dental fluorosis	Skeletal fluorosis	Crippling skeletal fluorosis
WHO, 1984	>1,5	3,0-6,0	>10
US, EPA	>2,0	--	>4,0
TANZANIA	-	>8,0	-
ARGENTINA, URBAN RURAL	>1,5 >2,2	-	-
Brouwer, *et al.*, 1988, TROPICS	>0,6	-	-

5.5 FACTORS THAT EFFECT THE DISTRIBUTION OF FLUORIDE IN GROUNDWATER

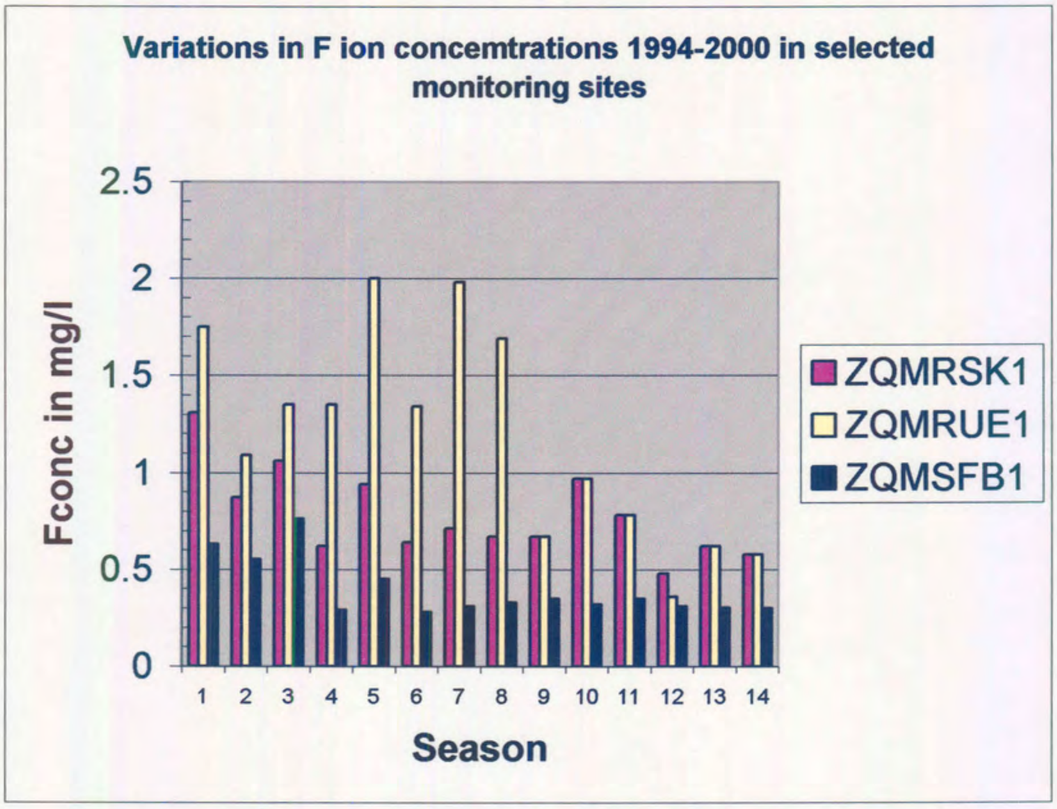
5.5.1 Introduction

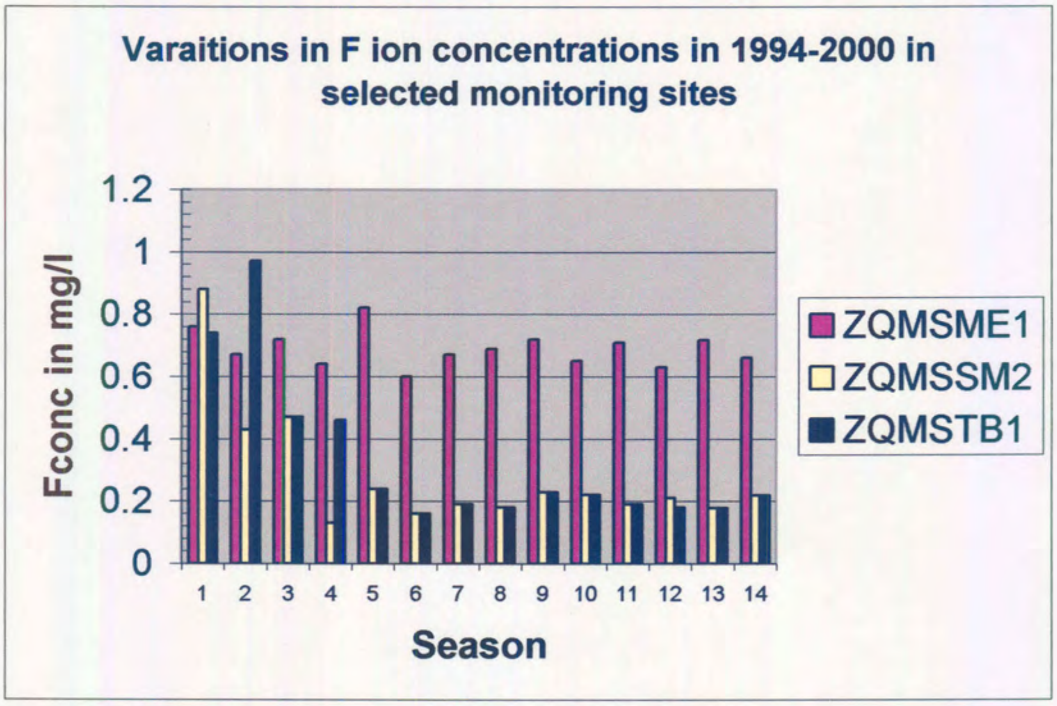
In a country such as South Africa with its extreme climatic variations between very wet and very dry seasons one might anticipate a variation in the fluoride content of the groundwater. If this were true it would be important not only to know the fluoride levels in groundwater used for drinking purposes but also the range of variation. The variation in fluoride content is considered to be the result of the interplay of a number of factors of which the more important are those discussed in detail in Chapter 2 of this dissertation. It is important to understand these factors in order to be able to properly manage fluoride in water resources. It was observed during this study that the fluoride levels in groundwater sources varied from one season to another and from one month to another. It was observed that in other sources the changes were minimal. This raised the interest of determining some of the factors that could contribute to this behaviour. These are the following;

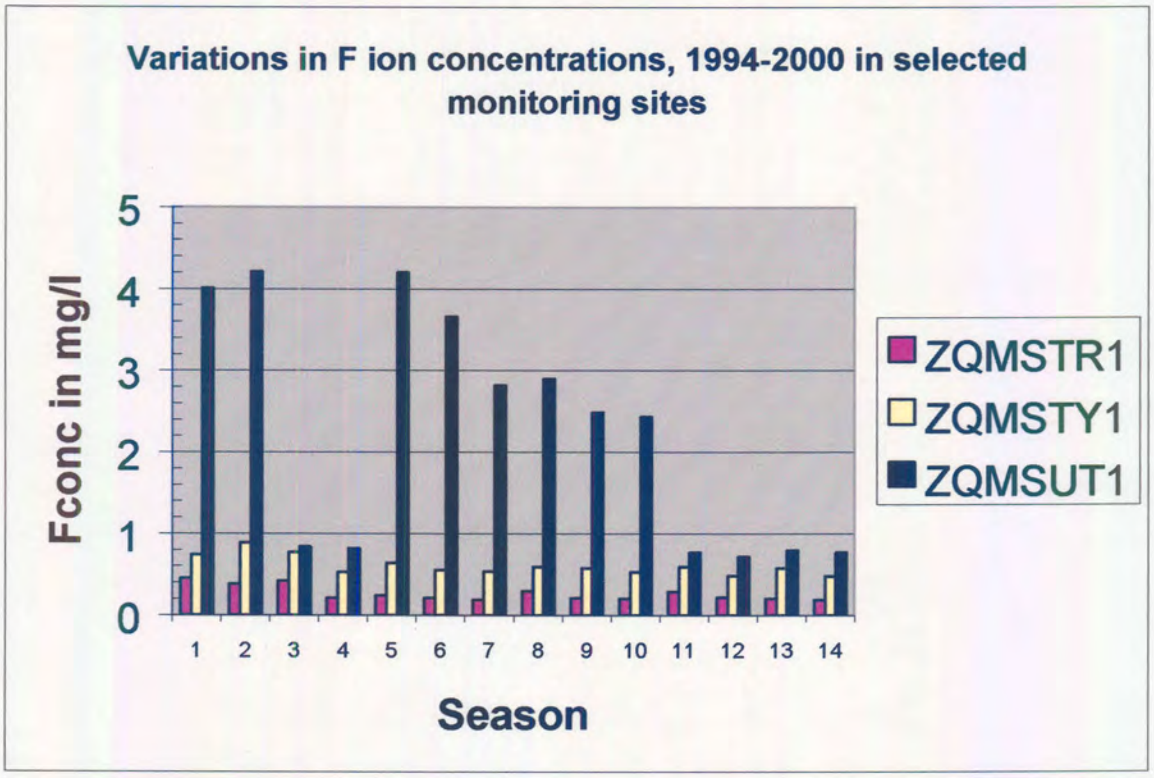
- The effect of climate, e.g. rainfall
- The role of other water quality parameters,
- The role of surface geology

5.5.2 The role of climate

A few boreholes were selected for this exercise. This included boreholes that were frequently monitored between 1994 and 2000. Three cases were selected, those with good quality drinking water, that is between 0-0,1; those with fluoride ion concentrations between 1,0 and 1,5 mg/ℓ and those sites with fluoride ion concentrations greater than 4 mg/ℓ and from which the consumption of their water for a long time presents a high risk for dental fluorosis. The boreholes selected were monitored between April 1994 and December 2000. For most of these sources sampling was done twice a year, before the rain season (for example in April) and after the rains (in October). The results are as presented below. However variations with time were not assessed. The rest of the graphs are as shown in Appendix A. Since the period runs over 7 years, 14 seasons were identified. Odd numbers represent the dry season while even numbers the wet season


Variations in F ion concemtrations 1994-2000 in selected monitoring sites
2.5
2
1.5
1
0.5
0
Fconc in mg/l
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Season
ZQMRSK1
ZQMRUE1
ZQMSFB1


Varaitions in F ion concentrations in 1994-2000 in selected monitoring sites
1.2
1
0.8
0.6
0.4
0.2
0
Fconc in mg/l
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Season
ZQMSME1
ZQMSSM2
ZQMSTB1



The results from the above graphs show the changes in fluoride concentration in different boreholes. While other boreholes show some variations, the borehole at ZQMSFB1 shows variations for the first 3 years and insignificant variation over the remaining years. This cannot however be assigned to the climate effect only.

Table 27 below shows such effect in three different sites. Climatic influences affect the fluoride concentrations in water considerably in areas with high levels of fluoride. It is observed from the results that during dry months the fluoride content increases and during and after the rains, the content goes down. However, it is very difficult to generalize from the observations since the pattern of variations changes from year to year in some cases. This is an indication that besides the climate, there are other factors that influence the level of fluoride ion concentrations in groundwater.

Table: 27: Effect of climate on fluoride levels in groundwater

Area	DS F in mg/l	WS F in mg/l	DS F in mg/l	WS F in mg/l	DS F in mg/l	WS F, mg/l
ZQMRSK1	1994	1994	1995	1995	1996	1996
Borehole 1	1,30	0,85	1,08	0,65	0,85	0,70
ZQMRUE1	1,74	1,10	1,34	1,32	2,00	1,35
ZQMSFB1	0,62	0,55	1,08	0,30	0,95	0,31

DS - Dry Season
WS - Wet Season

The above observations show that during the dry months, the water evaporates from the main rocks and soils that contain fluorides. This contributes to an increase in concentration as the various geological forms withhold the fluoride ion. More important is the fact of low inflow into aquifers. As a result the fluoride content increases. During and after the rains, the F^- content decreases owing to dilution. However that is not always the case in some boreholes. The rains promote chemical weathering and leaching of various rocks rich in fluoride. The fluoride rich water might be carried down the direction of flow increasing the fluoride levels at the final basins in which the water ends. The nature of variations observed raised the need to look into other possible contributors such as the interactions of the fluoride ion with other water quality parameters and the role played by the geology of the area.

5.5.3 Interactions of the F^- with other water quality parameters

5.5.3.1 Introduction

Due to the pronounced electron affinity of the fluorine atom, fluorine interacts with almost every element. It readily reacts with calcium to form the relatively insoluble calcium fluoride. Where phosphate is present an even more insoluble apatite or hydroxyapatite forms. In this study, Pearson's product- moment correlation was used to assess the nature of the associations.

This correlation assumes that the two variables are measured on at least two interval scales and it determines the extent to which values of the two parameters are "proportional" to each other. The correlations follow the following general expression:

$$Y = \mathbf{m}*F + C$$

Where, Y is the dependent variable, in this case any of the parameters interacting with the fluoride ion, **m**-is the slope of the proportionality line, C is the intercept on the Y-axis and F is the fluoride ion concentration.

Three sites were selected for this study, each with a different water composition. The data for the major inorganic parameters was downloaded from the WMS and the correlation graphs are shown in Appendix B. The results are shown in Table 28 below. The different associations between the fluoride ion and other parameters should be noted. For this exercise parameters of interest to the fluoride chemistry in water were considered (details in Chapter 3). In this dissertation, however only correlations between the fluoride ion and Total Alkalinity (TAL), pH, Mg, Ca, Si, EC, and PO_4-P were studied. Pearson product moment correlation using STATISTICA was used to assess the interactions. Correlations were considered significant at $p < 0,5$. Any coefficient between –0,2 and +0,2 was considered insignificant.

Table 28: Pearson correlation coefficients between fluoride and other parameters measured in three different sites.

Parameter	Borehole water in Steynberg, n =13	Borehole water at TUGELA, n =13	Borehole water in ZALEXBAY1, n=25
pH	-0.5057	-0.2200	-0.1800
Mg	-0.4412	+0.5336	+0.5724
Ca	-0.4273	+0.5351	+0.6339
Na	+0.2547	+0.1187	+0.6658
Si	-0.3772	+0.2407	-0.0924
Total Alkalinity	-0.0889	+0.1178	+0.7154
EC	+0.1183	-0.2300	+0.6800
PO4-P	-0.2371	-0.0.2219	-0.1794

+ correlation shows direct impact on the fluoride ion concentration

- correlation shows indirect impact on the fluoride ion concentration

Fluoride ion concentrations in natural waters have been found to depend on a number of factors. These include temperature, pH, presence or absence of complexing and precipitating ions, solubility of fluoride-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-), type of geological formations traversed by water and the amount of time that water is in contact with a certain geological formation as discovered by Apambire, *et al.*, 1997. This section presents a discussion on the correlations between fluoride and other water quality parameters as observed from the three boreholes that were selected for the study. However, the main source of F^- is most probably the dissolution of the various minerals of which the most important is fluorite, CaF_2. The inverse relationship between F and Ca and the positive relationship between F^- and HCO_3^- and F^- and Na are in agreement with the following equations:

$$CaF_2 + Na_2CO3 \rightarrow CaCO_3 + 2Na^+ + 2F^-$$

$$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O \text{ and } CO_2$$

5.5.3.2 Correlation of F with Hardness

Water hardness is commonly defined as the sum of the polyvalent cations dissolved in water. The most common such cations are calcium and magnesium, although iron, strontium and manganese may contribute. Hardness is usually reported as an equivalent quantity of calcium carbonate ($CaCO_3$). It is primarily a function of the geology of the area with which the water is associated. Waters underlain by limestone are likely to be hard because rainwater containing CO_2 continually dissolves the rock and carries the dissolved cations to the water system.

These metals can precipitate the fluoride ion as their respective fluorides. The levels of maximum possible calcium and magnesium in the presence of the fluoride ion in water is governed by the solubility principle. (Details in Chapter 2). The solubility products of calcium fluoride and magnesium fluoride are 3.9×10^{-11} and 6.4×10^{-9} $(mol/dm^{-3})^3$ respectively. The equilibrium for CaF_2 can be written as follows;

$CaF_2 \rightarrow Ca^{2+} + 2F^-$

$Ksp = [Ca^{2+}][F^-]^2$

$= 3.9 \times 10^{-11}\ mol^3dm^{-9}$

Similarly, for MgF_2 it will be;

$MgF_2 \rightarrow Mg^{2+} + 2F^-$

$Ksp = [Mg^{2+}][F^-]^2$

$= 6.4 \times 10^{-9}\ mol^3dm^{-9}$

This means that, only when the product of ionic concentrations of calcium and fluoride in water exceeds 3.9×10^{-11} and that of magnesium and fluoride exceeds 6.4×10^{-9} these salts will precipitate out. Otherwise, when the level of fluoride ion in groundwater increases levels of calcium or magnesium ions automatically decreases.

From the results, the correlation between F^- and Ca^{2+} depends strongly on the concentrations of the two ions. At lower concentrations for both ions the correlations are positive (Table 28). At high F^- concentrations and high Ca^{2+} concentrations the correlation was still positive (Table 28). At concentrations of F^- moderately high i.e. between 0,3 – 1,00 mg/ℓ the correlation was negative. (Table 28) This can be explained using the common ion effect. The dissolution of fluorite is suppressed when the concentration of Ca^{2+} is above the limit for fluorite solubility. A strong negative correlation between Ca^{2+} and F^- (-0,43) in groundwater that contain Ca^{2+} in excess of that required for the solubility of fluorite was shown (Table 28).

5.5.3.3 Correlation with Na^+

It is observed from the results that in groundwater with low Na^+ concentration, the fluoride content is generally in the range of 0,02 – 3,0 mg/l (Appendix B). Sodium exhibits a positive correlation with fluoride in many types of groundwater, especially those having low concentrations of calcium (waters undergoing base exchange). High concentrations of Na^+ will increase the solubility of fluorite in waters. This can lead to very high concentrations of fluoride in water.

The results showed moderate to s between Na^+ and F^- irrespective of the concentrations of other water quality parameters in any of the boreholes. It can be concluded that Na^+ has a direct influence on the concentrations of the fluoride ion in groundwater and plays a significant role in increasing the solubility of fluorine containing minerals such as fluorite (Table 28).

5.5.3.4 Correlation between pH and F^-

The correlation was generally negative and not significant. The pH of the water is controlled by the equilibrium achieved by dissolved compounds in the system. In natural waters, the pH is primarily a function of the carbonate system, which is composed of carbon dioxide, CO_2, carbonic acid, H_2CO_3 bicarbonate, HCO_3^- and carbonate, CO^{2-}_3. The applicable equilibrium equations and the estimated pH ranges at which are present are:

$CO_2 + H_2O \longrightarrow H_2CO_3$	pH <6.4	
$H_2CO_3 \longrightarrow H^+ + HCO^-_3$	pH: 6.4 - 10.33	Ka_1
$HCO^-_3 \longrightarrow H^+ + CO_3^{2-}$	pH: >10.3	Ka_2

A process that can also lead to very high concentrations of fluoride in waters and little understood is the anion exchange (OH^- for F^-) involving various types of clay minerals. This process invariably follows base exchange softening (Ca^{2+} and Mg^{2+} for Na^+) where the pH is progressively driven to quite high alkaline values (pH 9.0 - 10.5). Anion exchange can occur in sedimentary basins (Boyle and Chagnon, 1995) or igneous terrain but it is most dominant in the sedimentary basins. The relationship of pH and fluoride in groundwater is explained in detail in **Chapter 2.**

5.5.3.5 Correlation between fluoride and Phosphate

The results show negative correlation between the two species. The natural inorganic phosphorus deposits occur primarily as phosphate in the mineral apatite. Apatite is defined as natural, variously coloured calcium fluoride phosphate ($Ca_5F(PO4)_3$) with chlorine, hydroxyl and carbonate sometimes replacing the fluoride. Apatite is found in igneous, metamorphic and sedimentary rocks.

Phosphate deposits and phosphate rich rocks release phosphorus during weathering, erosion and leaching **(Chapter 2).** Apatite is widely distributed in all rock types; igneous, sedimentary and metamorphic but is just in small grains, large well-formed crystals though can be found in certain contact metamorphic rocks. Apatite is actually three different minerals depending on the predominance of fluorine, chlorine or the hydroxyl group. These ions can freely substitute in the crystal lattice and all three are usually present in every specimen although some specimens:$Ca_5(PO_4)_3(OH,F,CI)$, Calcium(Fluoro,ChloroHydroxyl) Phosphate (WRC, 2001).

5.5.3.6 Correlation between Fluoride and Total Alkalinity

The results in Table 28 show positive correlation between the Total Alkalinity and fluoride levels. This might be due to the release of hydroxyl and bicarbonate ions simultaneously during the leaching and dissolution process of fluoride bearing minerals into the groundwater. That is more and more leaching of minerals into water increases the fluoride ion concentration with high levels of alkalinity as well. High fluoride levels are associated with the high concentration of sodium ions because of greater solubility of sodium fluoride in water. Similarly, high levels of sodium are associated with increased concentration of bicarbonate ions also and this naturally leads to higher alkalinity levels. The correlation between silicate and the electrical conductivity are not discussed in this dissertation. However, the theory is presented in the literature survey.

5.5.4 The role of surface geology

High fluoride levels are mainly found in areas underlain by sedimentary rocks, granites, metamorphic and volcanic rocks (Maps A and B). In the Northern Cape this is mainly in the areas underlain by consolidated to compact sedimentary data, porous unconsolidated to semi-consolidated sedimentary strata and compact sedimentary strata. In North-West province levels higher than the recommended upper limit for drinking water are observed mainly in areas underlain by porous unconsolidated to semi-consolidated sedimentary strata, dolomite chert and subordinate limestone and assemblage of compact sedimentary and extrusive rocks. These are observed in the case of other provinces except for the compact arenaceous and argillaceous strata and the mafic basic lavas that show in the KwaZulu Natal and Limpopo. A detailed and in-depth description of the role of surface geology is however beyond the scope of this dissertation.

It is evident from the above observations that the occurrence and the observed distribution of fluoride ion concentrations in groundwater are largely dependent on the geology of the area. The geochemistry also plays an important role in understanding the behavior of fluorides. The tables in Appendix D show the content of fluoride in various rock types.

From the results of this study, it has been observed that high fluoride levels are mainly found in areas underlain by sedimentary rocks, granites, metamorphic and volcanic rocks This shows that the phenomena of high fluoride levels in groundwater is linked to the geology of the area. However, this cannot always be traced to geological formations as the water may come in contact with different fluorine-bearing formations kilometres away from these rocks.

Fluorine becomes a component of sedimentary rocks through several processes. Fluorine may be present in resistant minerals as topaz, tourmalite and apatite and to a lesser extent fluorite and the micas. It may be absorbed onto an anion receptor such as a clay particle, or it may be transported into the sediment as an aqueous ion or complex. In marine sediments it may co-precipitate from seawater with $CaCO_3$ and phosphate. In sediments, F is highest in clay–bearing rocks such as shales and mudstones, (Appendix D) although some sandstone has become cemented by fluorite. In limestones, some CaF_2 and MgF_2 co-precipitate with $CaCO_3$, but most F is found as fluorapatite in the skeletal remains of marine organisms. In gypsum, F co-precipitates with $CaSO_4$ as CaF_2, but the inability of F to precipitate as Na or K compounds is reflected in the very low concentrations in rock salt. This can be the case in those coastal areas with high fluoride ion content in their groundwater. (MAPS A1-A3)

No detailed study or field investigations were carried out to determine the cause of the high fluoride levels observed in various regions of the country for this dissertation. The interpretation of the results is based on the observations made after the data was overlain on Vegter's lithostratigraphy and the use of some South African geological maps. A detailed description of the role of geology in the occurrence and distribution of fluoride is given in Chapter 2.

CHAPTER 6: CONCLUSIONS

- Areas with high fluoride ion concentrations in their groundwater supplies and high percentage morbidity of dental fluorosis have been identified. Many of these sources require partial de-fluoridation if they are currently used for drinking water purposes or the development of alternative water supplies as a matter of urgency.

- Areas of low fluoride ion concentrations in groundwater have been delineated. In view of the DOH Regulations tabulated in September 2000, such areas are in need of fluoridation.

- Fluorides are found in almost all geological forms but high levels are mainly found in areas underlain by sedimentary rocks, granites, and metamorphic and volcanic rocks. This shows that the occurrence of high fluoride levels in groundwater is linked to the geology of the area and that chemical leaching (weathering) of the rocks and their associates are important fluoride contributors. However, this origin cannot only be traced to surface geology as other factors also play a role (**Chapter 2**).

    - The release of the fluoride ion into groundwater depends on a number of factors. These include the solubility of the mineral in which the fluorine atom is found, the pH, the climate, the hardness and the chemical characteristics of the groundwater. Correlations exist between the fluoride ion and Mg, Ca, Na, Total Alkalinity and silica. The moderate positive correlation between fluoride and silica suggests that there may be a contribution of fluoride to the groundwater from the decomposition of fluorosilicates. However the results reflect that the main source of high fluoride ion concentration in groundwater is most probably the dissolution of fluorite, CaF_2. Given the strong correlations between Na and fluorite in some boreholes, it is evident that the presence of sodium ions plays a significant role in increasing the dissolution and hence the solubility of fluorine containing minerals especially fluorite in groundwater.

- A weak correlation between fluoride ion concentration in groundwater and the percentage morbidity of dental fluorosis has been shown in some areas. This phenomena could be due to a number of factors among which the differences of the calcium content in the diet of various individuals, variations of fluoride levels in groundwater caused by different geographical conditions in which boreholes are found, injection of fluorides into the hydrological cycle by various industrial activities, socio-economic factors, etc can be mentioned.

CHAPTER 7 RECOMMENDATIONS

From the findings of this study, it is recommended that

- Proper research need to be initiated into investigating cheap and technological simple processes for small scale removal of fluoride from fluoride-rich groundwater or developing alternative methods of water supply in areas where there is such a problem especially in rural areas.

- Combined efforts between the National Department of Health and the Department of Water Affairs and Forestry in determining the fluoridation/de-fluoridation strategies are initiated. It is not practical to fluoridate boreholes; natural springs or hand dug wells on which most of the rural areas depend on. Extensive research into alternative methods of fluoridation such as salt fluoridation, milk fluoridation, sugar fluoridation and use of fluoride supplements such as fluoride drops, fluoride lozenges, fluoridated toothpaste, fluoridated vitamins, etc need to be initiated in affected areas.

- Since the delineation of the high-risk areas, with fluoride levels beyond recommended levels for drinking water have clearly been done in this document, it is recommended that those requiring the upgrading of water supplies and the identification of fluorosis risk areas utilize this document. The installation of future boreholes should be accompanied by simple and suitable de-fluoridation techniques. Awareness programmes to educate the public about the consequences of drinking fluoride-rich waters must be in place.

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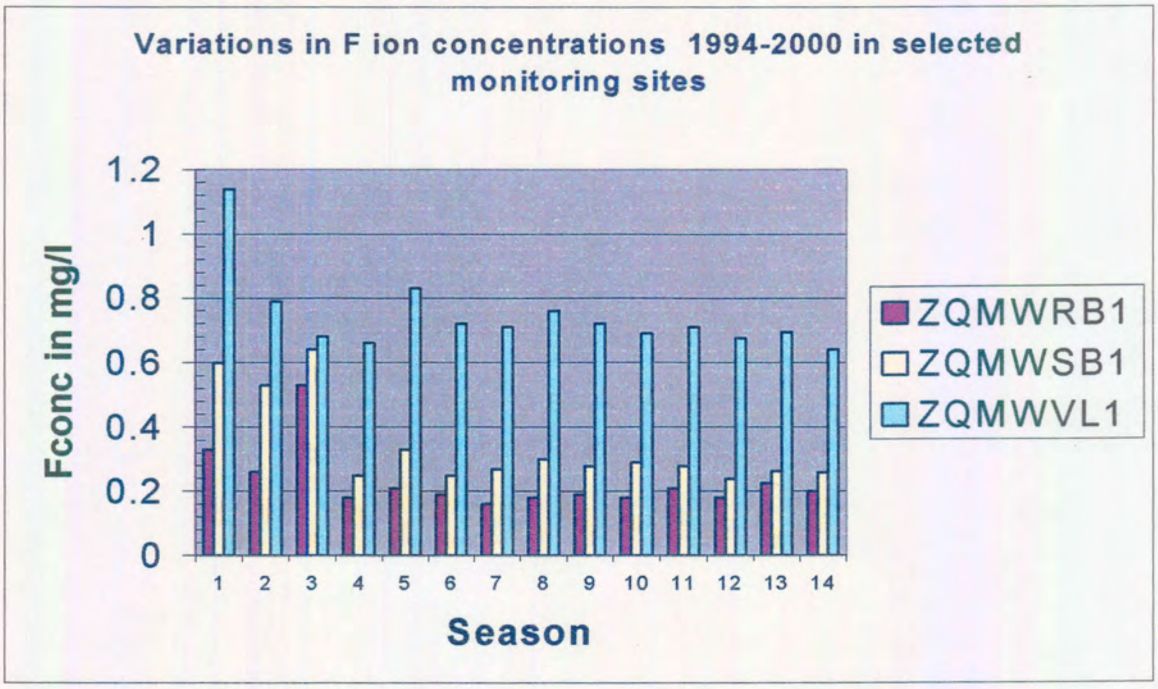
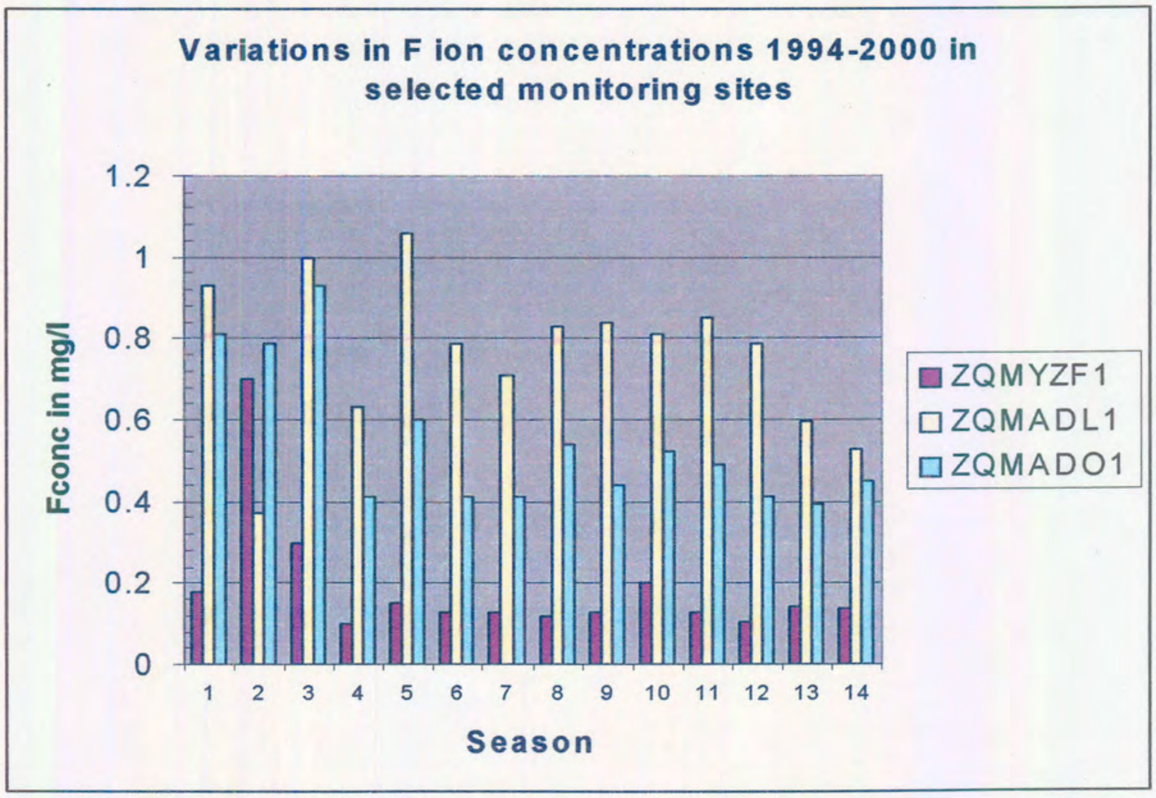
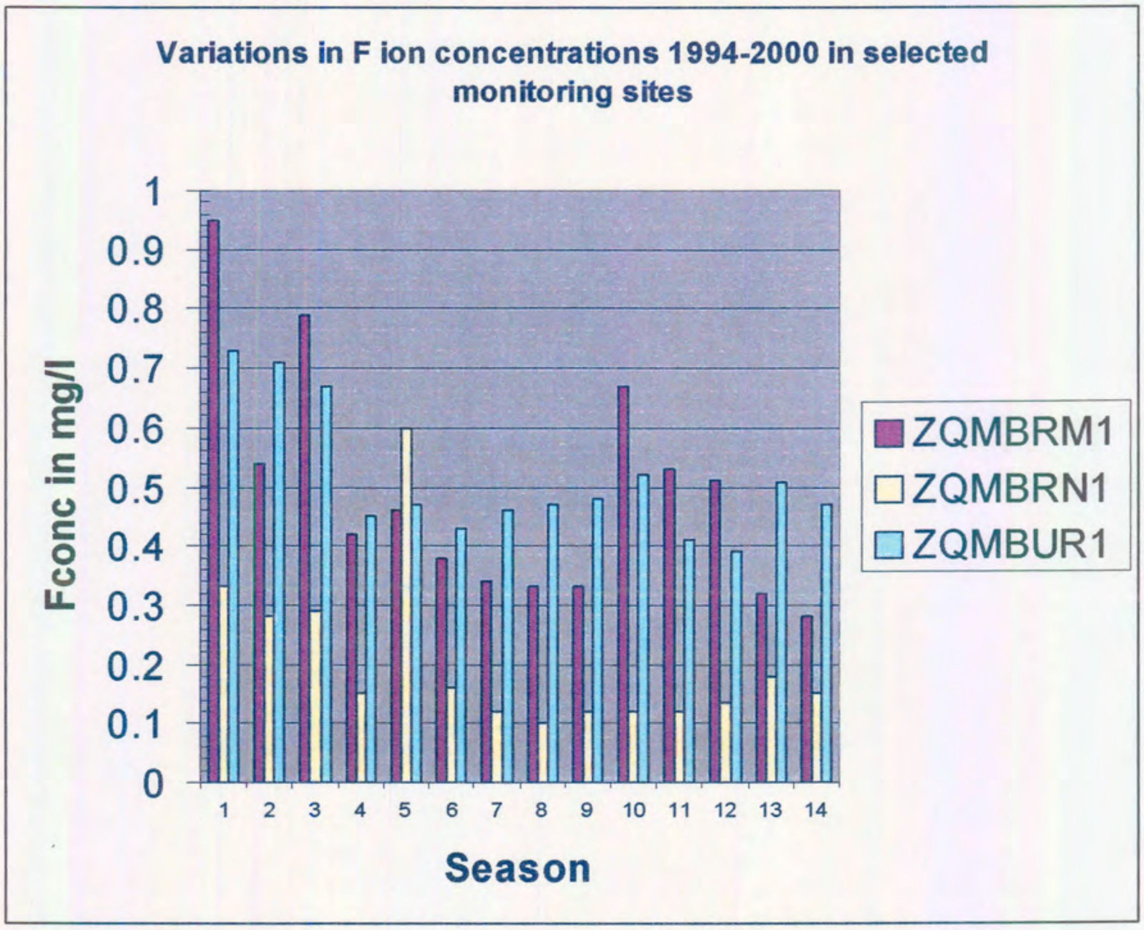
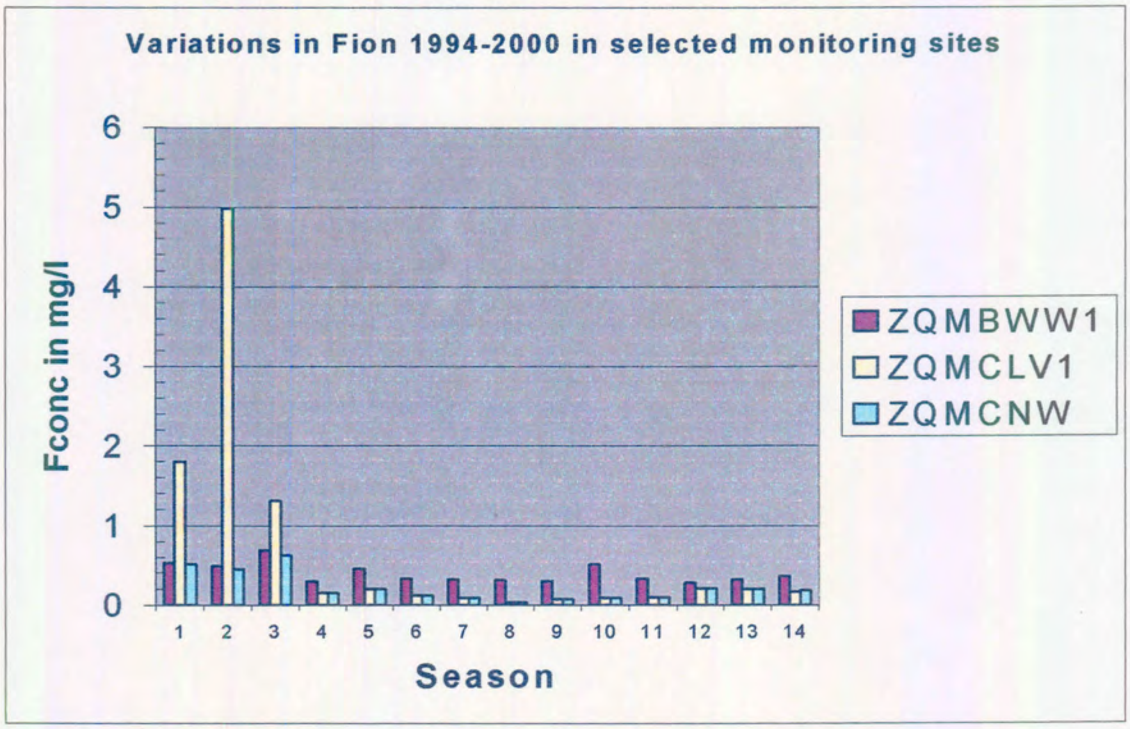
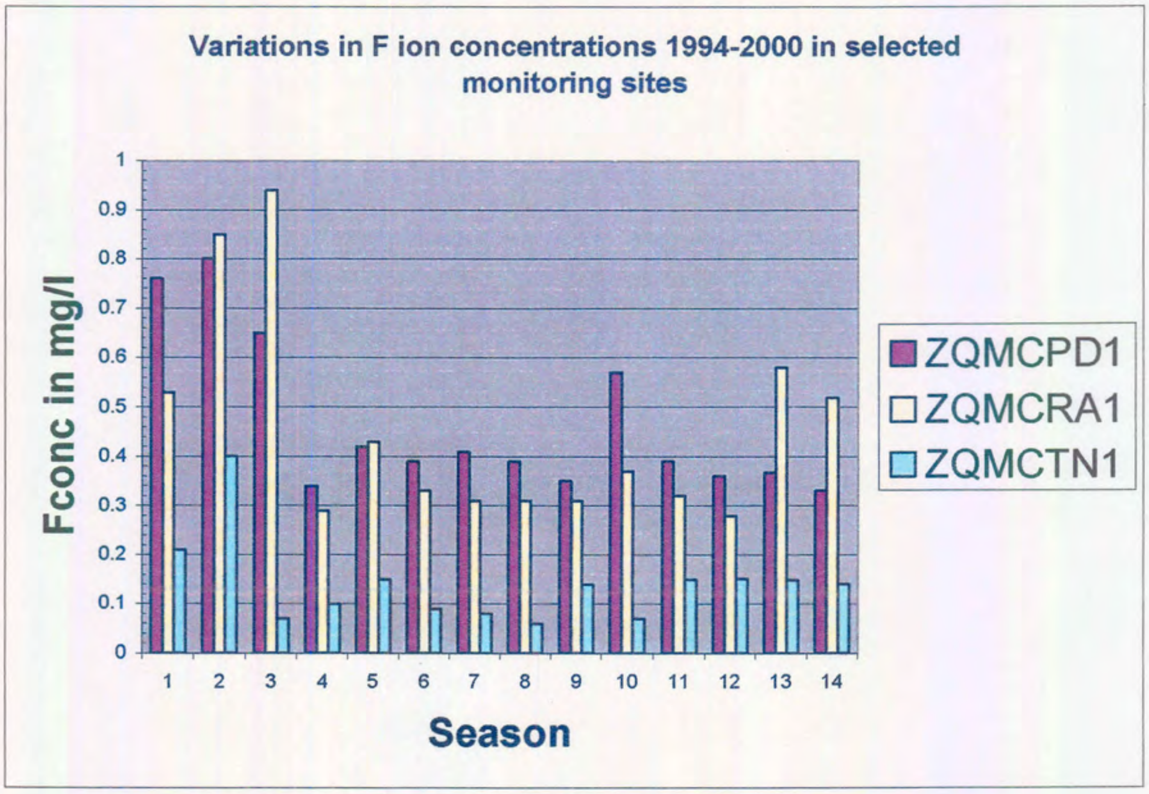
APPENDIX A VARIATIONS OF FLUORIDE ION CONCENTRATIONS IN SELECTED BOREHOLES, 1994-2000

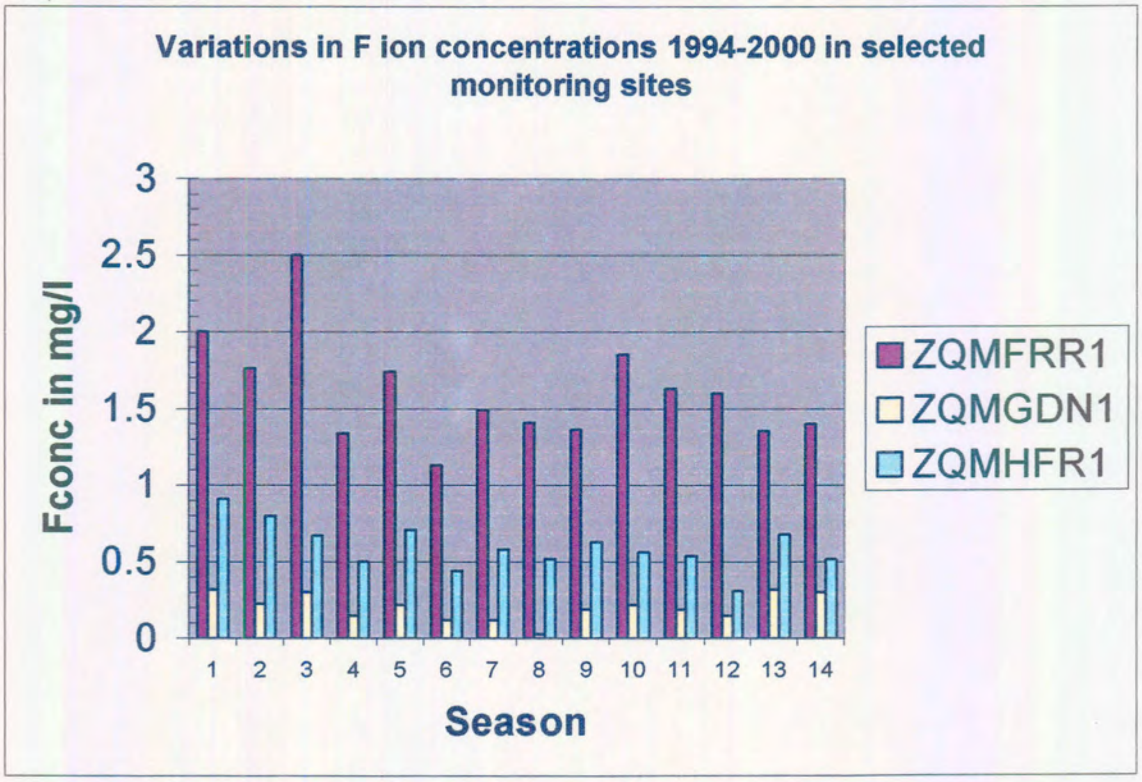

Variations in F ion concentrations 1994-2000 in selected monitoring sites
Fconc in mg/l
1.2
1
0.8
0.6
0.4
0.2
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Season
ZQMWRB1
ZQMWSB1
ZQMWVL1

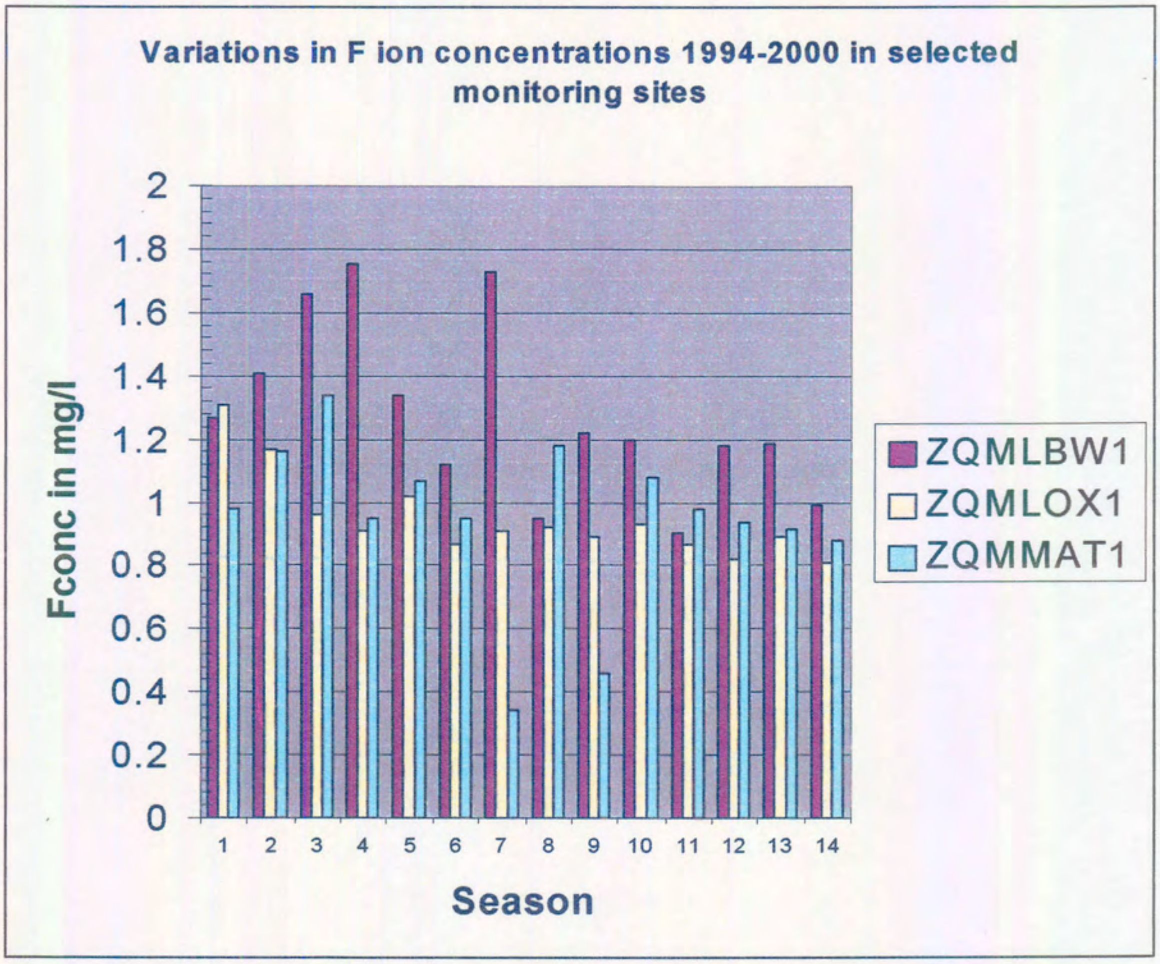

Variations in F ion concentrations 1994-2000 in selected monitoring sites
Fconc in mg/l
1.2
1
0.8
0.6
0.4
0.2
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Season
ZQMYZF1
ZQMADL1
ZQMADO1


Variations in F ion concentrations 1994-2000 in selected monitoring sites
Fconc in mg/l
Season
ZQMBRM1
ZQMBRN1
ZQMBUR1


Variations in Fion 1994-2000 in selected monitoring sites
Fconc in mg/l
Season
ZQMBWW1
ZQMCLV1
ZQMCNW


Variations in F ion concentrations 1994-2000 in selected monitoring sites
Fconc in mg/l
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Season
ZQMCPD1
ZQMCRA1
ZQMCTN1


Variations in F ion concentrations 1994-2000 in selected monitoring sites
Fconc in mg/l
0
0.5
1
1.5
2
2.5
3
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Season
ZQMFRR1
ZQMGDN1
ZQMHFR1


Variations in F ion concentrations 1994-2000 in selected monitoring sites
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Fconc in mg/l
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Season
ZQMLBW1
ZQMLOX1
ZQMMAT1

APPENDIX B: CORRELATION STUDIES OF THE FLUORIDE ION AND OTHER WATER QUALITY PARAMETERS

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Monitoring Feature ID: 88493 name: ZALEXBAYI BOREHOLE AT OPPEINHEIMER BRID
Latitude: -28.566111 Drainage Region: D First date: 18/03/1997
Longitude: 16.508056 n=25 Last date 2001/05/02

DATA FROM A BOREHOLE AT OPPEINHEIMER BRID

[redacted]

0.307	14.102	4.481	37.031	36.231	35.580	60.736	0.018	8.440	128.289	0.625	347.73	6.540	51.400	0.020
0.282	11.521	3.966	32.969	34.421	34.474	49.029	0.020	8.100	120.660	0.460	315.92	5.531	45.600	0.020
0.272	14.631	3.464	39.470	37.840	39.041	53.535	0.035	8.230	133.450	0.195	352.15	5.557	51.930	0.020
0.250	14.809	3.566	38.151	38.600	38.379	43.800	0.017	8.210	142.530	0.126	352.16	4.452	50.500	0.020
0.275	15.750	2.985	36.600	40.100	41.850	51.600	0.018	8.250	141.150	0.059	361.50	5.900	51.050	0.017
0.285	19.450	3.610	45.500	47.170	55.020	86.950	0.019	8.300	134.200	0.099	422.25	6.090	61.550	0.086
0.320	22.400	4.500	50.800	55.200	64.300	102.300	0.021	8.310	142.800	0.105	474.00	6.440	68.800	0.009
0.382	16.952	3.698	38.364	52.971	47.700	46.910	0.024	8.570	155.350	0.141	397.11	4.140	57.450	0.020
0.294	15.100	3.808	37.540	36.800	34.080	60.960	0.015	8.310	131.340	0.152	349.00	4.620	50.540	0.019
0.285	15.450	4.200	39.350	37.450	34.050	67.850	0.016	8.280	132.150	0.148	360.00	4.790	52.750	0.018
0.275	13.475	3.495	34.675	37.650	32.850	51.050	0.024	8.080	121.550	0.172	325.00	5.107	46.200	0.031
0.217	11.530	2.760	29.700	31.467	23.333	37.133	0.016	8.140	111.630	0.312	272.67	5.860	39.700	0.027
0.217	15.133	2.607	35.767	37.400	42.433	39.333	0.021	8.420	131.200	0.105	333.67	5.320	48.133	0.028
0.230	16.200	2.805	39.000	43.900	49.700	42.050	0.021	8.210	132.250	0.091	350.50	6.835	51.350	0.011
0.218	12.700	2.380	31.025	34.350	35.600	32.950	0.018	8.320	117.900	0.208	294.00	4.452	42.800	0.057
0.280	12.820	2.310	32.520	32.920	36.775	32.800	0.017	8.250	119.800	0.156	297.00	4.765	43.250	0.032
0.230	15.240	2.765	35.980	40.040	44.320	38.440	0.017	8.450	144.160	0.074	353.20	4.410	50.340	0.015
0.240	11.740	2.545	29.450	26.050	22.150	32.350	0.008	8.340	121.850	0.303	274.50	6.320	38.650	0.031
0.210	11.000	2.790	29.200	24.550	17.250	34.450	0.013	8.170	110.750	0.495	257.00	6.215	37.600	0.023
0.210	10.600	2.270	28.600	20.800	14.200	35.200	0.059	8.180	100.000	0.499	236.00	5.740	35.200	0.061
0.220	11.150	3.385	28.400	24.700	15.710	40.350	0.048	8.220	103.900	0.547	253.50	5.220	38.400	0.054
0.222	11.950	2.640	28.650	22.450	20.950	37.250	0.009	8.350	99.900	0.069	246.00	2.340	35.750	0.020
0.243	13.580	2.790	32.140	28.340	28.660	40.440	0.007	8.320	116.080	0.072	288.00	3.030	42.220	0.025
0.380	16.830	3.650	41.770	41.830	45.970	46.900	0.015	8.530	146.170	0.129	376.00	3.640	53.970	0.022
0.330	14.050	3.490	36.900	37.600	32.800	42.250	0.011	8.350	150.400	0.098	351.00	5.490	50.800	0.012

CORRELATION COEFFICIENTS at $p<0.05$

1.000	0.572	0.667	0.634	0.666	0.547	0.467	-0.179	0.508	0.715	-0.230	0.689	-0.092	0.684	-0.283
0.572	1.000	0.537	0.959	0.902	0.924	0.803	-0.170	0.411	0.735	-0.568	0.952	0.123	0.953	-0.146
0.667	0.537	1.000	0.666	0.561	0.438	0.762	-0.048	0.134	0.482	0.089	0.670	0.164	0.691	-0.279
0.634	0.959	0.666	1.000	0.891	0.903	0.841	-0.126	0.307	0.759	-0.465	0.970	0.205	0.976	-0.184
0.666	0.902	0.561	0.891	1.000	0.944	0.659	-0.160	0.370	0.847	-0.501	0.956	0.178	0.949	-0.234
0.547	0.924	0.438	0.903	0.944	1.000	0.651	-0.215	0.375	0.776	-0.573	0.932	0.145	0.924	-0.185
0.467	0.803	0.762	0.841	0.659	0.651	1.000	-0.014	0.061	0.398	-0.179	0.795	0.286	0.815	0.016
-0.179	-0.170	-0.048	-0.126	-0.160	-0.215	-0.014	1.000	-0.265	-0.289	0.454	-0.183	0.234	-0.141	0.437
0.508	0.411	0.134	0.307	0.370	0.375	0.061	-0.265	1.000	0.527	-0.296	0.376	-0.354	0.370	-0.155
0.715	0.735	0.482	0.759	0.847	0.776	0.398	-0.289	0.527	1.000	-0.529	0.849	0.070	0.824	-0.412
-0.230	-0.568	0.089	-0.465	-0.501	-0.573	-0.179	0.454	-0.296	-0.529	1.000	-0.481	0.407	-0.446	0.252
0.689	0.952	0.670	0.970	0.956	0.932	0.795	-0.183	0.376	0.849	-0.481	1.000	0.194	0.996	-0.226
-0.092	0.123	0.164	0.205	0.178	0.145	0.286	0.234	-0.354	0.070	0.407	0.194	1.000	0.207	0.076
0.684	0.953	0.691	0.976	0.949	0.924	0.815	-0.141	0.370	0.824	-0.446	0.996	0.207	1.000	0.076
-0.283	-0.146	-0.279	-0.184	-0.234	-0.185	0.016	0.437	-0.155	-0.412	0.252	-0.226	0.076	-0.202	1.000

Monitoring Feature ID: 89775 name: ZQMTUG2 TUGELA BAD
Latitude: -22.569167 Drainage Region: A63 First date: 95/06/27
Longitude: 28.621944 n=13 Last date: 2001/01/05

DATA FROM A BOREHOLE AT TUGELA BAD

	F	Mg	K	Ca	Na	Cl	SO4	PO4-P	pH	TAL	NO3	DMS-TOT	Si	EC	NH4-N
1	1.242	1.357	8.540	128.973	359.175	298.973	237.136	0.019	8.24	32.569	0.147	1075.64	34.163	250.000	0.080
2	4.787	<1	8.689	422.205	324.000	422.205	513.106	0.017	7.73	32.309	0.256	1452.41	38.989	238.000	0.052
3	5.212	<1	8.771	415.205	370.425	415.205	500.074	0.028	8.07	33.362	<0.04	1461.00	36.636	232.000	0.048
4	4.650	1.500	8.760	417.600	356.900	417.600	534.700	0.034	8.09	34.000	0.077	1508.00	30.340	229.000	0.090
5	4.950	<1	9.470	447.700	413.800	447.700	550.100	0.014	8.74	25.000	0.054	1585.00	33.210	236.000	0.046
6	5.600	<1	8.330	405.500	369.400	405.500	483.500	0.014	8.23	42.600	0.115	1454.00	37.370	240.000	0.062
7	5.650	<1	8.390	394.600	379.000	394.600	485.100	0.014	7.70	56.900	<0.04	1469.00	41.610	2.600	0.070
8	5.010	<1	8.020	386.600	367.500	386.600	463.200	0.012	8.10	43.500	0.055	1408.00	32.960	220.000	0.078
9	4.800	<1	8.820	400.300	370.200	400.300	487.000	0.013	8.70	27.000	<0.04	1434.00	33.200	223.000	0.049
10	5.320	<1	8.550	398.500	376.700	398.500	525.500	0.013	7.57	31.000	0.139	1486.00	34.320	220.000	0.057
11	4.950	<1	8.260	392.600	361.200	392.600	484.900	0.005	8.80	21.700	0.040	1409.00	32.800	260.000	<0.04
12	4.980	1.600	8.260	406.600	373.900	406.600	525.600	0.015	8.08	16.700	0.088	1460.00	35.440	2.600	<0.04
13	5.594	6.830	8.150	128.193	338.786	403.684	488.800	0.007	7.61	22.786	<0.04	1408.03	34.019	248.000	<0.04

CORRELATIION COEFFICIENTS at $p<0.05$

	F	Mg	K	Ca	Na	Cl	SO4	PO4-P	pH	TAL	NO3	DMS-TOT	Si	EC-Phys	NH4-N
F	1.000	0.534	-0.118	0.535	0.119	0.804	0.870	-0.222	-0.216	0.118	-0.212	0.850	0.241	-0.229	-0.383
Mg	0.534	1.000	-0.683	-0.551	-0.837	0.295	0.232	-0.694	-0.972	-0.329	-0.843	0.185	0.166	0.334	1.000
K	-0.118	-0.683	1.000	0.349	0.468	0.393	0.223	0.392	0.384	-0.171	-0.071	0.339	-0.131	0.225	-0.521
Ca	0.535	-0.551	0.349	1.000	0.395	0.686	0.711	0.211	0.241	0.143	-0.182	0.757	0.122	-0.211	-0.445
Na	0.119	-0.837	0.468	0.395	1.000	0.215	0.196	-0.031	0.443	0.059	-0.662	0.351	-0.107	-0.249	-0.257
Cl	0.804	0.295	0.393	0.686	0.215	1.000	0.955	0.069	0.026	-0.141	-0.122	0.962	0.042	-0.057	-0.507
SO4	0.870	0.232	0.223	0.711	0.196	0.955	1.000	0.015	-0.070	-0.143	-0.175	0.975	0.008	-0.176	-0.412
PO4-P	-0.222	-0.694	0.392	0.211	-0.031	0.069	0.015	1.000	-0.117	0.182	0.164	0.056	-0.104	0.028	-0.354
pH	-0.216	-0.972	-0.216	0.241	0.443	0.026	-0.070	-0.117	1.000	-0.340	-0.670	-0.010	-0.456	0.280	-0.227
TAL	0.118	-0.329	-0.171	0.143	0.059	-0.141	-0.143	0.182	-0.336	1.000	0.172	-0.015	0.540	-0.225	0.429
NO3	-0.212	-0.843	0.071	-0.182	-0.662	-0.122	-0.175	0.164	-0.673	0.172	1.000	-0.228	0.749	0.105	-0.312
DMS-Tot	0.850	0.185	0.339	0.757	0.351	0.962	0.975	0.056	-0.010	-0.015	-0.228	1.000	0.045	-0.179	-0.413
Si	0.241	0.166	-0.131	0.122	-0.107	0.042	0.008	-0.104	-0.456	0.540	0.749	0.045	1.000	-0.507	-0.292
EC-Phys	-0.229	0.334	0.225	-0.211	-0.249	-0.057	-0.176	0.028	0.280	-0.225	0.105	-0.179	-0.507	1.000	-0.143
NH4-N	-0.383	1.000	-0.521	-0.445	-0.257	-0.507	-0.412	0.354	-0.227	0.429	-0.312	-0.413	-0.292	-0.143	1.000

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YUNIBESITHI YA PRETORIA

Monitoring Feature ID:	89740	Name:	ZQMSTB1 STEYNSBURG		DORPSGEBIED
Latitude:	-31.29611	Drainage Region Q12		Start date:	21/04/1994
Longitude:	25.830278	n=13		Last date:	28/05/2001

DATA FROM A BOREHOLE AT STEYNSBURG

pH	NO3+NO2	F	TAL	Na	Mg	Si	PO4-P	SO4	Cl	K	Ca	EC (mS/m)	DMS-Tot
7.971	1.073	0.397	281.468	113.401	29.162	10.105	0.014	192.198	130.675	0.941	114.902	127.800	929.708
8.129	3.058	0.400	267.822	125.108	23.936	9.575	0.011	183.039	117.076	0.694	97.528	119.900	887.921
7.35	3.740	0.740	322.200	129.300	19.100	10.570	0.014	149.200	98.000	0.350	102.200	107.900	908.000
7.35	2.820	0.970	297.800	135.800	21.500	9.040	0.008	146.300	103.400	1.260	97.600	119.500	882.000
8.01	1.783	0.470	313.600	138.300	20.100	10.690	0.009	160.100	101.200	1.510	98.900	114.700	911.000
8.29	1.648	0.430	329.900	146.000	23.400	10.450	0.016	178.200	96.900	1.790	107.400	131.400	964.000
8.02	2.115	0.560	323.400	132.700	18.400	9.290	0.006	156.900	94.000	1.290	92.500	1116.000	900.000
8	1.453	0.400	287.900	140.300	20.000	10.000	0.011	178.100	106.900	0.700	108.400	106.400	912.000
7.75	1.697	0.390	321.500	130.600	23.400	9.850	0.007	167.900	102.500	0.710	112.800	114.900	938.000
7.3	2.848	0.380	311.200	126.400	23.200	10.880	0.013	172.800	104.500	0.750	110.300	129.000	931.000
7.7	3.582	0.320	332.300	112.400	44.500	15.980	0.011	204.300	123.100	0.720	120.600	130.200	1027.000
7.9	1.904	0.390	329.800	130.200	23.600	10.090	0.009	182.900	108.800	0.670	121.600	126.100	979.000
7.86	4.380	0.390	337.400	137.000	30.500	10.020	0.017	229.700	148.600	0.700	159.900	150.300	1138.000

CORRELATION COEFFICIENTS at $p < 0.05$

	pH	NO3+NO2	F	TAL	Na	Mg	Si	PO4-P	SO4	Cl	K	Ca	EC (mS/m)	DMS-Tot
pH	1.000	-0.473	-0.506	-0.121	0.254	-0.014	-0.134	0.058	0.315	0.097	0.451	0.009	0.199	0.087
NO3+NO2	-0.473	1.000	0.183	0.313	-0.143	0.362	0.309	0.338	0.308	0.401	-0.443	0.419	-0.089	0.490
F	-0.506	0.183	1.000	-0.089	0.255	-0.441	-0.377	-0.237	-0.679	-0.386	0.160	-0.427	0.118	-0.444
TAL	-0.121	0.313	-0.089	1.000	0.215	0.229	0.348	0.099	0.179	-0.042	0.082	0.442	0.174	0.612
Na	0.254	-0.143	0.255	0.215	1.000	-0.632	-0.528	0.027	-0.263	-0.391	0.482	-0.063	0.061	-0.036
Mg	-0.014	0.362	-0.441	0.229	-0.632	1.000	0.825	0.280	0.718	0.654	-0.168	0.537	-0.249	0.633
Si	-0.134	0.309	-0.377	0.348	-0.528	0.825	1.000	0.142	0.373	0.217	-0.101	0.209	-0.203	0.381
PO4-P	0.058	0.338	-0.237	0.099	0.027	0.280	0.142	1.000	0.559	0.514	-0.101	0.548	-0.438	0.524
SO4	0.315	0.315	-0.386	0.179	-0.263	0.718	0.373	0.559	1.000	0.887	-0.250	0.861	-0.232	0.859
Cl	0.097	0.401	0.401	-0.042	-0.391	0.654	0.217	0.514	0.887	1.000	-0.349	0.814	-0.288	0.733
K	0.451	-0.443	0.160	0.082	0.482	-0.212	0.217	-0.101	-0.250	-0.349	1.000	-0.338	0.270	-0.188
Ca	0.009	0.419	-0.427	0.442	-0.063	0.537	0.209	0.548	0.861	0.814	-0.338	1.000	-0.293	0.948
EC (mS/m)	0.199	-0.089	0.118	0.174	0.061	-0.249	-0.203	-0.438	-0.232	-0.288	0.270	-0.293	1.000	-0.167
DMS-Tot	0.087	0.490	-0.444	0.612	-0.036	0.633	0.381	0.524	0.859	0.733	-0.188	0.948	-0.167	1.000

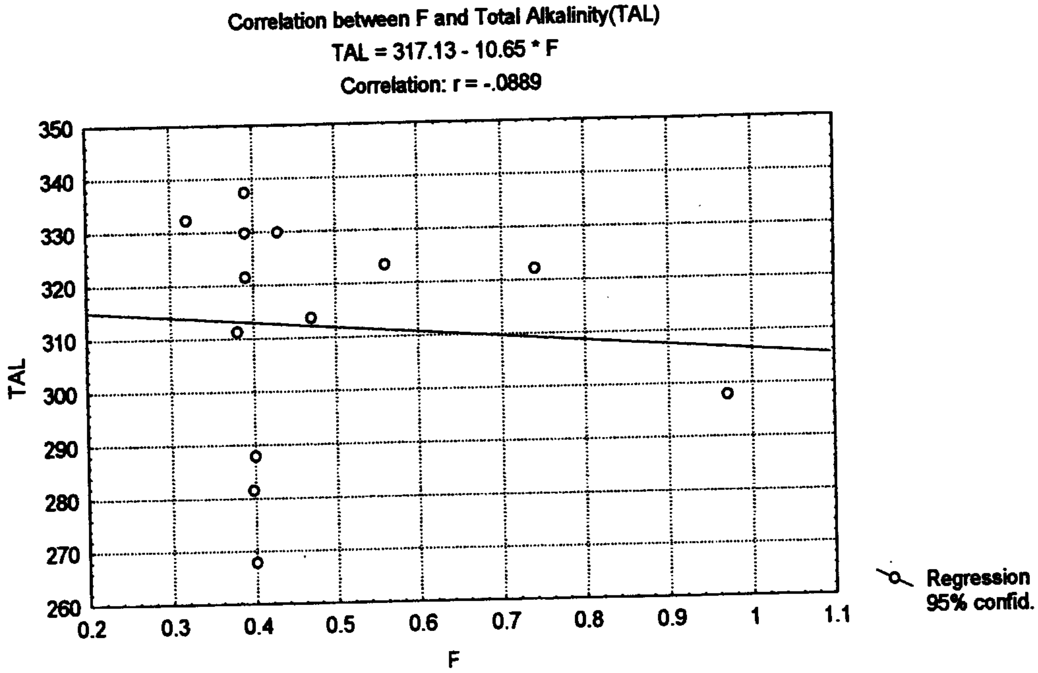


Fig The effect of Total Alkalinity on the fluoride ion concentration s in borehole water at Steynberg.

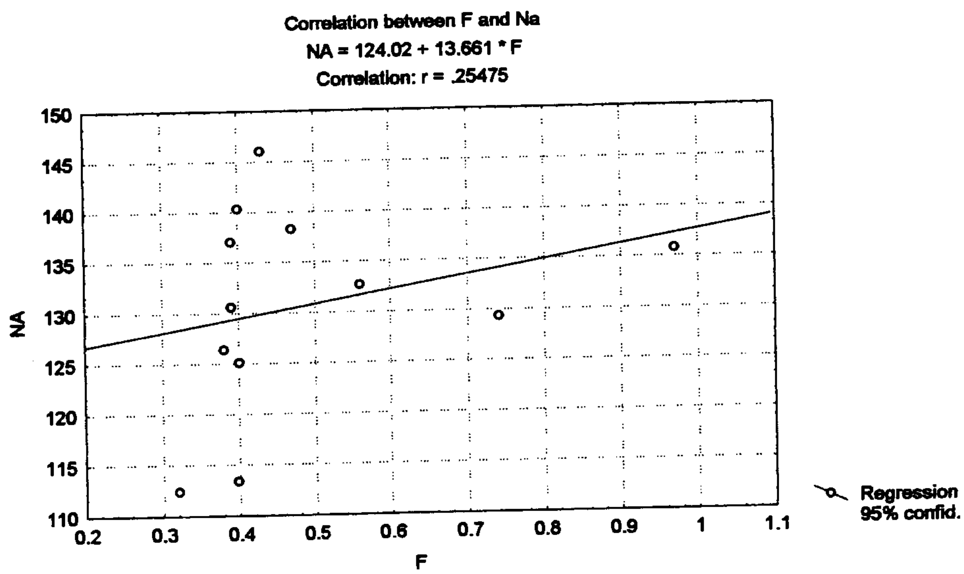


Fig The effect of sodium ion concentration on the fluoride ion concentration in borehole water at Steynberg

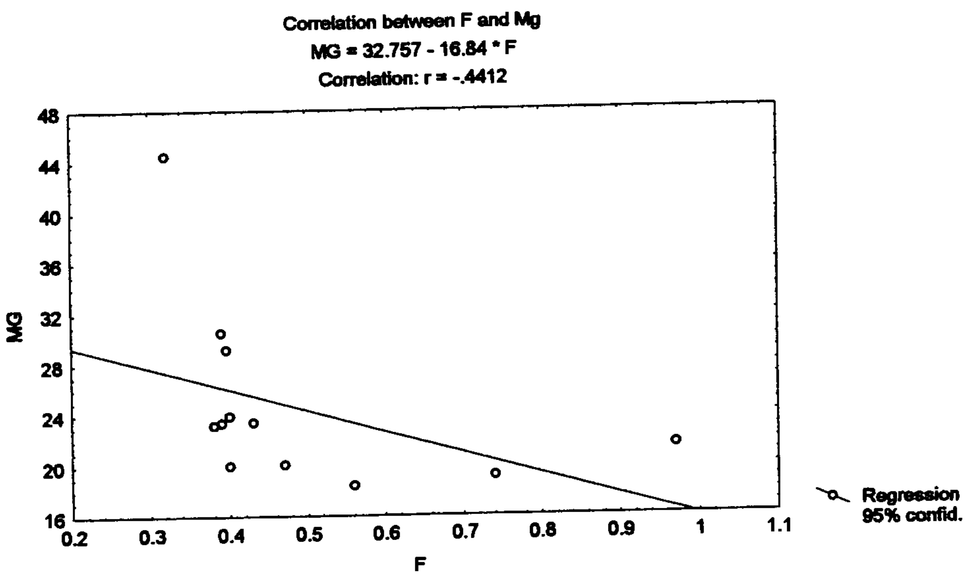


Fig The effect of Hardness(Mg ion concentration) on F ion concentration in borehole water at Steynberg

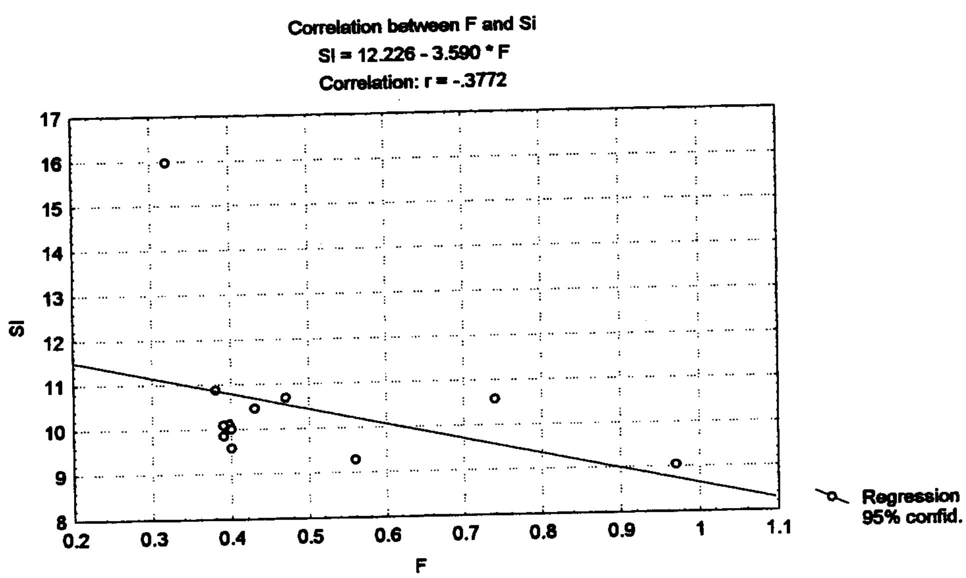


Fig The effect of silicate on the fluoride ion concentration in borehole water at Steynberg

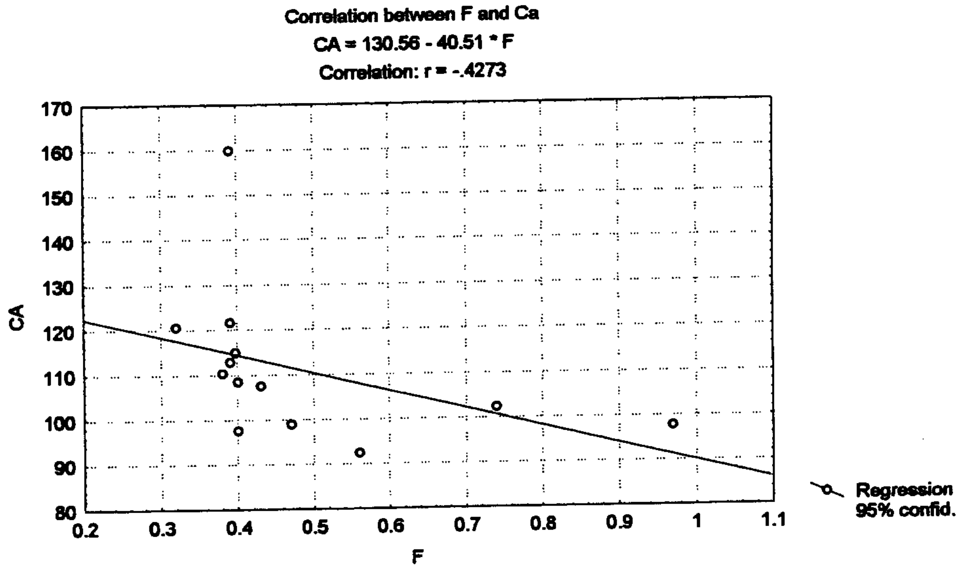


Fig The effect of Hardness (Calcium ion concentration) on fluoride ion concentration in borehole water at Steynberg

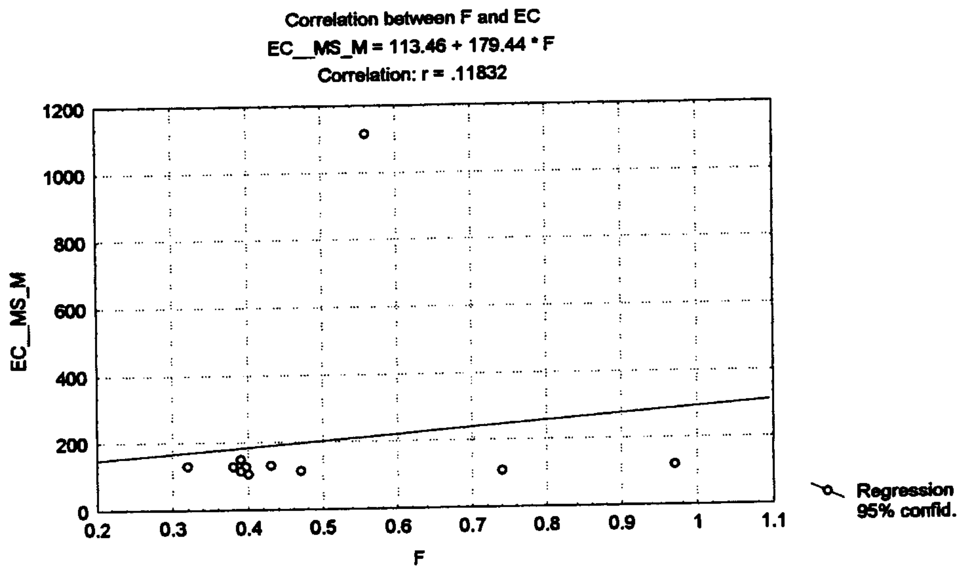


Fig The effect of Electrical Conductivity on fluoride ion concentration in borehole water at Steynberg.

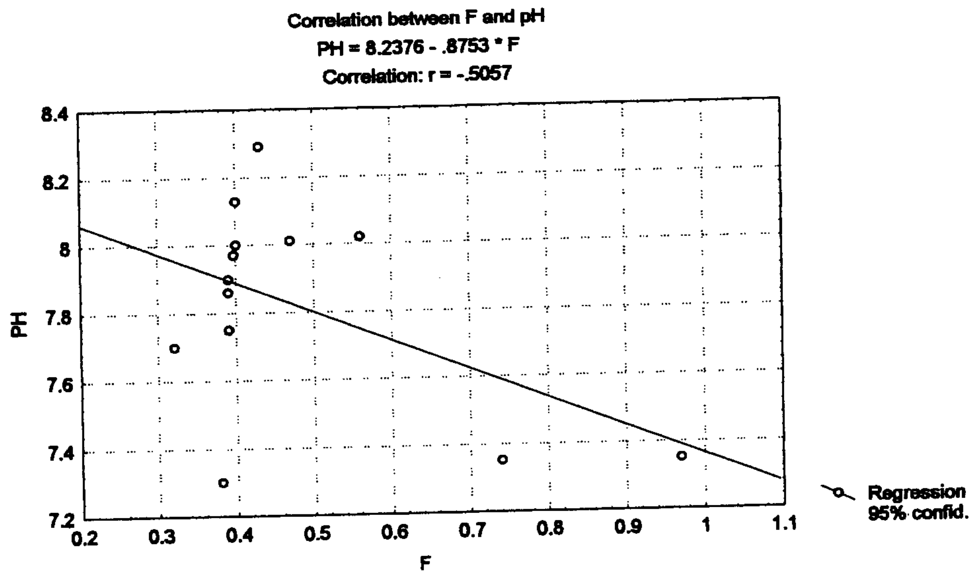


Fig The effect of pH on the fluoride ion concentrations in borehole water at Steynberg

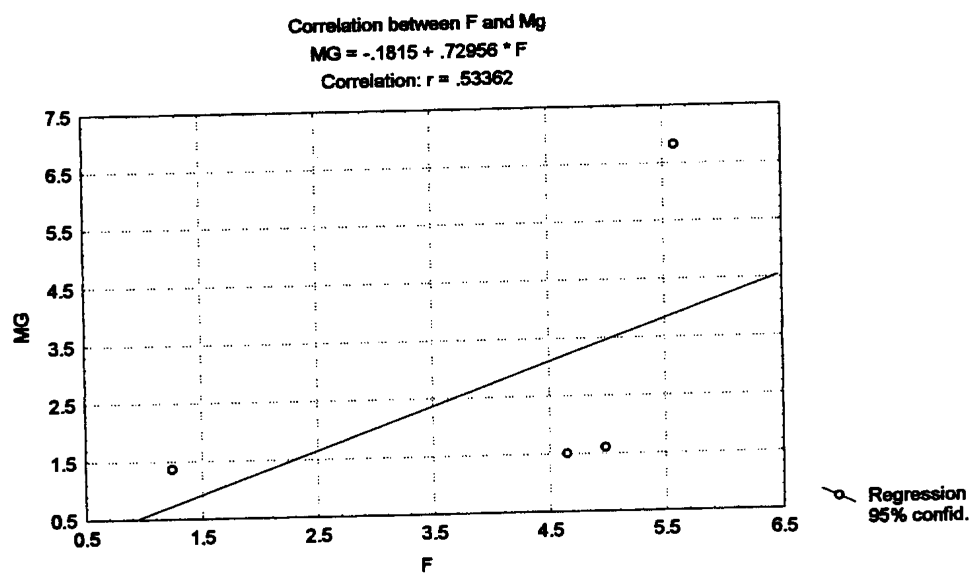


Fig The effect of Hardness(Mg ion concentration) on the fluoride ion concentrations in in a borehole along the TUGELA

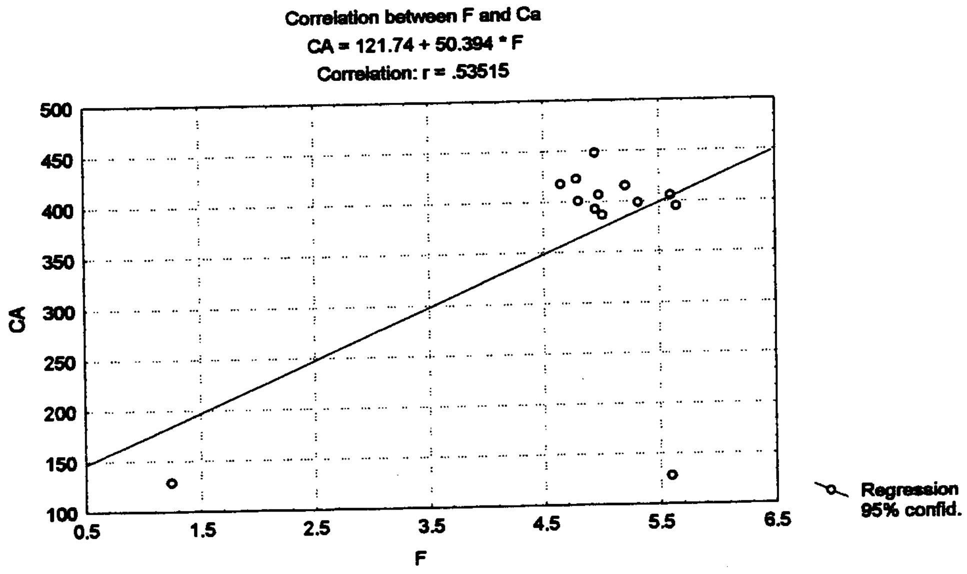


Fig The effect of Hardness (Ca ion concentration) on the fluoride ion concentration in a borehole along the TUGELA

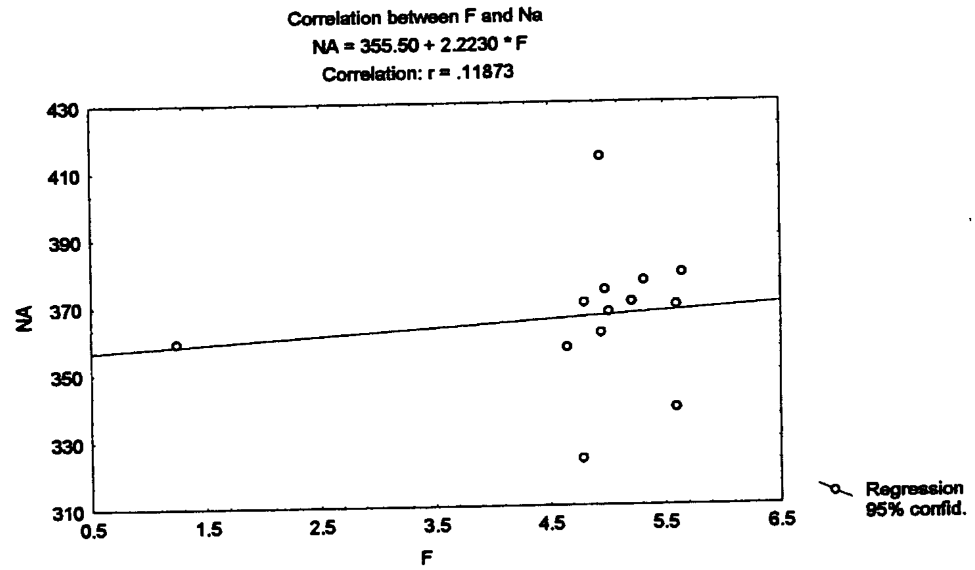
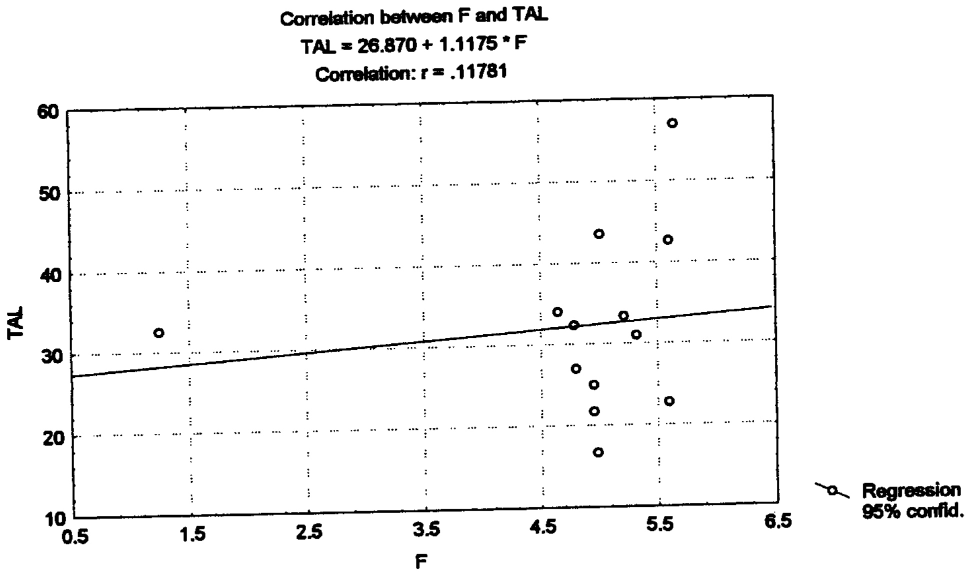


Fig The effect of Na ion concentration on fluoride ion concentration in a borehole along the TUGELA



The effect of Total Alkalinity on fluoride ion concentration in a borehole along the TUGELA

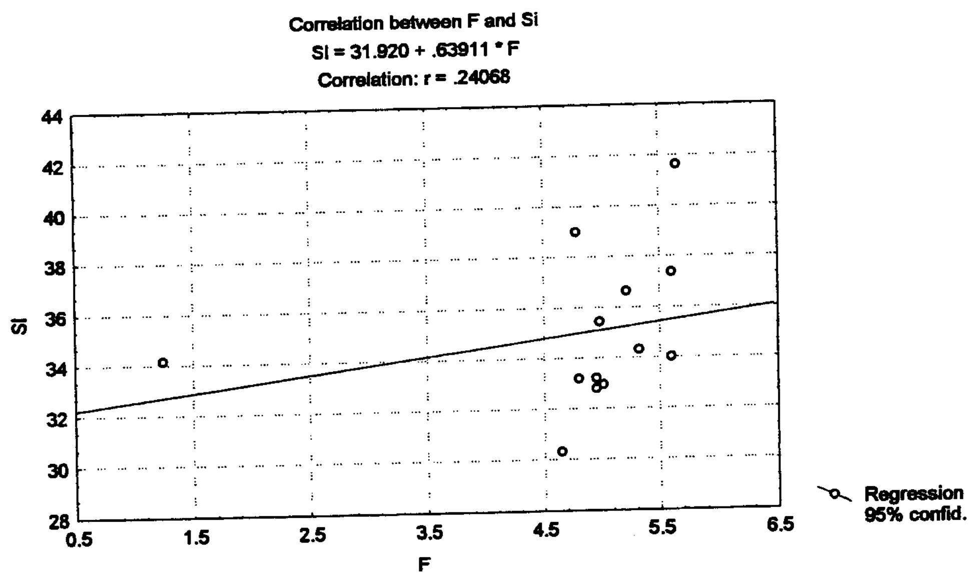


Fig The effect of silicate on fluoride ion concentration in a borehole along the TUGELA

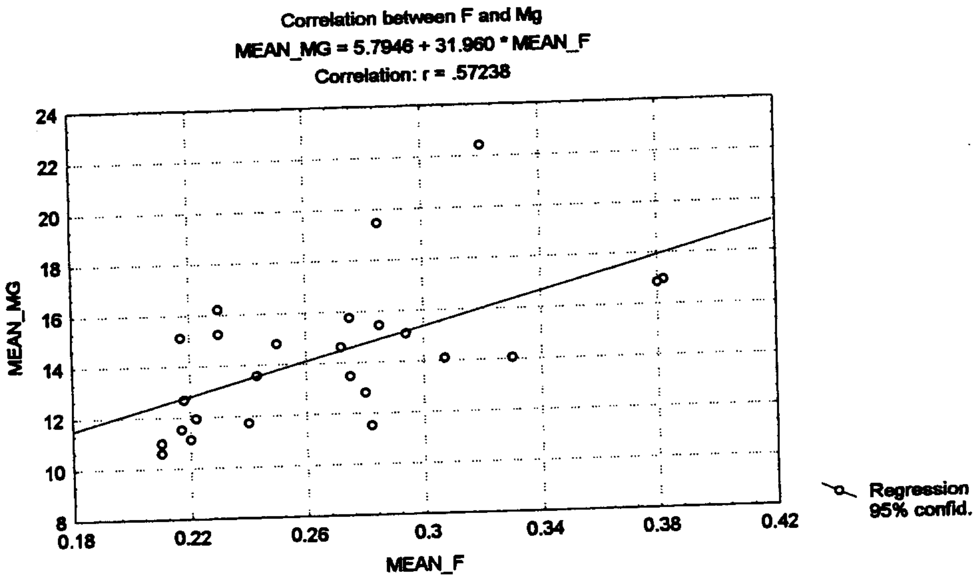


Fig The effect of Hardness (Mg ion concentration) on fluoride ion concentration in borehole water at ZALEXBAY1

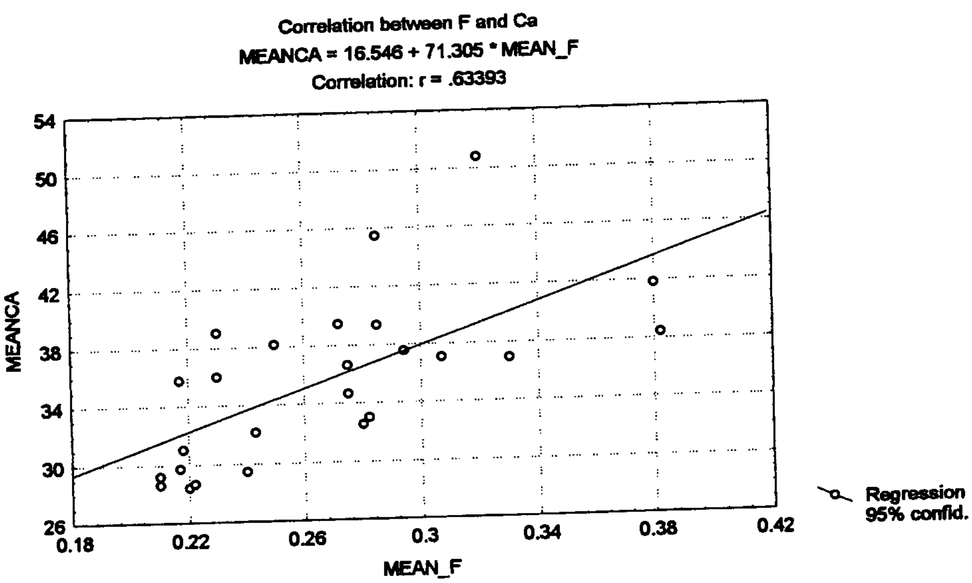


Fig The effect of Hardness (Ca ion concentration) on the fluoride ion concentration in borehole water at ZALEXBAY1

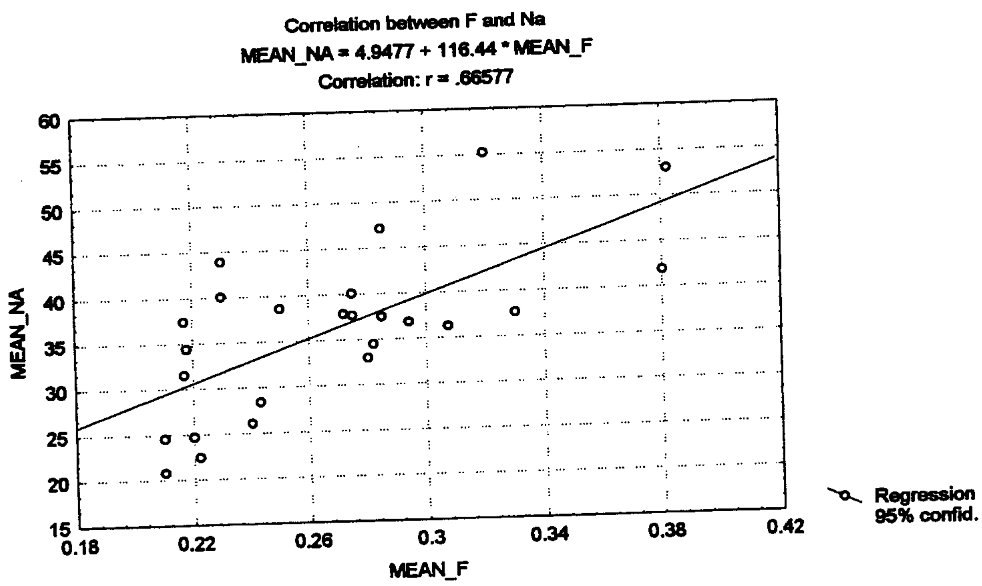


Fig The effect of Na ion concentartion on fluoride ion concentration in borehole water at ZALEXBAY1

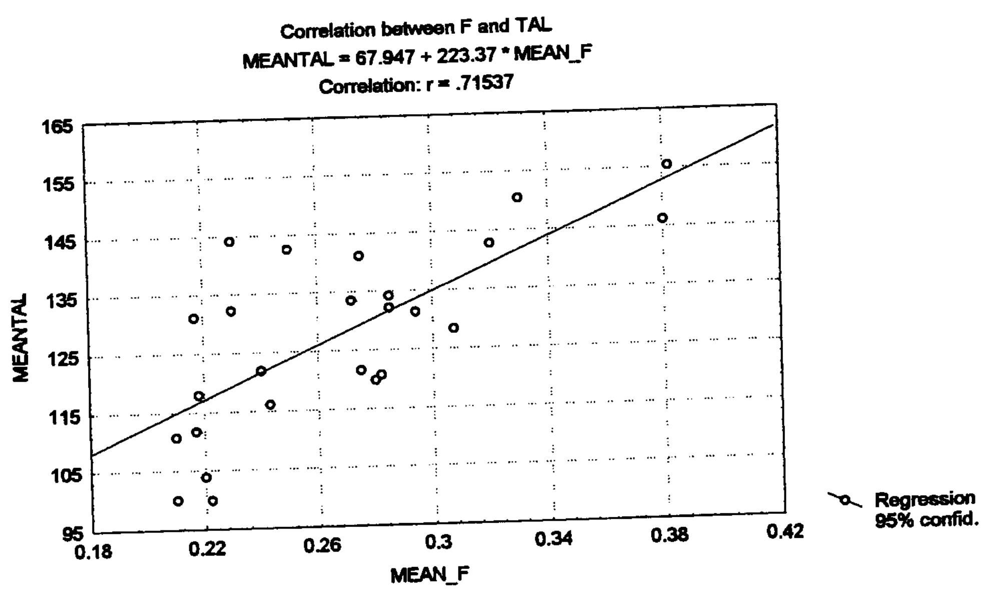


Fig The effect of Total Alkalinity on fluoride ion concentration in borehole water at ZALEXBAY1

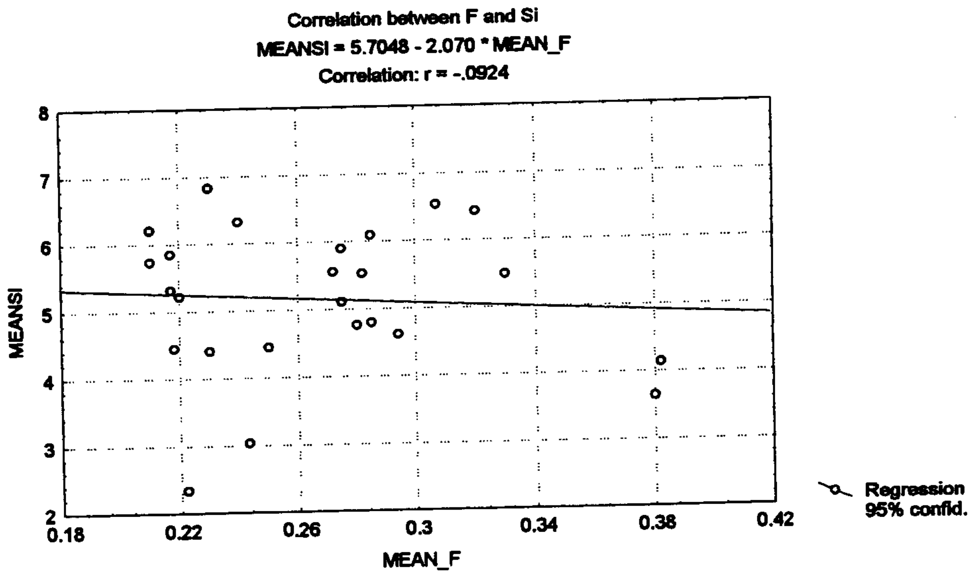


Fig The effect of silicate on fluoride ion concentration in borehole water at ZALEXBAY1

N.B Pearson Product moment correlation was used for the study. Marked correlations are significant at $p < 0.05$ n=13, 13 and 25 respectively.

APPENDIX C : OPTIMUM FLUORIDE ION CONCENTRATIONS FOR DRINKING WATER CALCULATED FOR THE REPUBLIC OF SOUTH AFRICA, 1985-1999

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OPTIMUM FLUORIDE LEVELS FOR 1985-1999, RSA 0.34 0.16 0.011

Cape Town, D.F Malan	211790	22.4	0.8366	22.2	0.8412	21.9	0.8481	22.08	0.8439
George P.W. Botha	286904	21.6	0.8551	21.7	0.8528	21.9	0.8481	21.4	0.8599
East London	595729	23.6	0.8103	23.2	0.8189	23.2	0.8189	20.8	0.8745
Jan Smuts/Johannesburg Int.	0476398A3	22.9	0.8254	22.7	0.8299	22.8	0.8277	22.1	0.8435
Port Elizabeth-Wk	351795	23.1	0.8211	22.7	0.8299	22.6	0.8321	22.3	0.8389
Louis Botha/ Durban	0240808A/0240808A2	25.8	0.8211	25.4	0.7738	25.2	0.7777	25.2	0.7777
Bloemfontein JBM Hertzog	2615161	25.1	0.7661	25.2	0.7796	25	0.7816	24.8	0.7856
Kimberly	0290468A9	26.6	0.7796	26.7	0.7494	26.7	0.7494	24.9	0.7836
Uppington	3174741	28.9	0.7114	28.9	0.7114	29.1	0.7082	28.1	0.7248
Bethlehem	3315859	22.7	0.8299	22.1	0.8435	22.4	0.8366	21.4	0.8599
Pretoria	0513314AX/C9	25.4	0.7738	25.3	0.7757	25.3	0.7757	25	0.7816
Nelspruit-Friedenheim	5558665	26.8	0.7476	26.8	0.7476	26.5	0.753	26.6	0.7512
Pietersburg	0677802A5/0677802BX	25.1	0.7796	25.1	0.7796	25.1	0.7796	24.7	0.7876

Cape Town, D.F Malan	211790	21.8	0.8504	21.6	0.8551	21.7	0.8528	21.4	0.8599
George P.W. Botha	286904	21.3	0.8623	21.2	0.8647	21.6	0.8551	21.3	0.8623
East London	595729	23.2	0.8189	22.8	0.8277	23.5	0.8124	24.6	0.7896
Jan Smuts/Johannesburg Int.	0476398A3	19.8	0.8999	22	0.8458	22.4	0.8366	23.8	0.7896
Port Elizabeth-Wk	351795	22.4	0.8366	22.2	0.8412	22.8	0.8277	22.4	0.8061
Louis Botha/ Durban	0240808A/0240808A2	25.2	0.7777	24.9	0.7836	25.6	0.7699	26.3	0.7567
Bloemfontein JBM Hertzog	2615161	24	0.8019	25.1	0.7796	24.3	0.7957	24.5	0.7916
Kimberly	0290468A9	25.9	0.7642	26.5	0.753	25.8	0.7661	27.5	0.7351
Uppington	3174741	28.1	0.7248	28.9	0.7114	28.4	0.7197	31.5	0.6713
Bethlehem	3315859	21.4	0.8599	22.3	0.8389	22.1	0.8435	23.4	0.8146
Pretoria	0513314AX/C9	24.6	0.7896	25.2	0.7777	25.2	0.7777	26	0.7623
Nelspruit-Friedenheim	5558665	26.6	0.7512	26.5	0.753	27	0.744	28	0.7265
Pietersburg	0677802A5/0677802BX	24.7	0.7876	25	0.7816	25.2	0.7876	-	

[redacted]

Cape Town, D.F Malan	211790	22.4	0.8366	22.4	0.8366	22.2	0.8412	21.6	0.8551
George P.W. Botha	286904	21.6	0.8551	21.6	0.8551	21.1	0.8671	21.6	0.8551
East London	595729	23.6	0.8103	23.9	0.804	23.4	0.8146	23	0.8232
Jan Smuts/Johannesburg Int.	0476398A3	22.8	0.8277	21.9	0.8481	22.4	0.8366	21.8	0.8504
Port Elizabeth-Wk	351795	22.6	0.8321	22.2	0.8412	21.8	0.8504	22.4	0.8366
Louis Botha/ Durban	0240808A/0240808A2	26	0.7623	25.4	0.7738	24.8	0.7856	24.9	0.7836
Bloemfontein JBM Hertzog	2615161	25.3	0.7757	24.6	0.7896	25	0.7816	23.8	0.8061
Kimberly	0290468A9	26.4	0.7549	26.4	0.7549	26.6	0.7549	25.3	0.7757
Uppington	3174741	30	0.6939	29.3	0.705	29.2	0.705	28	0.7265
Bethlehem	3315859	22.3	0.8389	21.9	0.8481	22	0.8481	20.6	0.8795
Pretoria	0513314AX/C9	26	0.7623	25.1	0.7796	25.1	0.7796	24.6	0.7896
Nelspruit-Friedenheim	5558665	27	0.744	25.2	0.7777	26.5	0.7777	26.3	0.7567
Pietersburg	0677802A5/0677802BX			25.3	0.7757	25.6	0.7757	24.6	0.7896

[redacted]

Cape Town, D.F Malan	211790	22.4	0.8366	22.5	0.8344	23.4	0.8146
George P.W. Botha	286904	21.7	0.8528	21.9	0.8481	22.6	0.8321
East London	595729	22.8	0.8277	23.5	0.8124	24.3	0.7957
Jan Smuts/Johannesburg Int.	0476398A3	21.7	0.8528	22.4	0.8366	22.2	0.8412
Port Elizabeth-Wk	351795	22.2	0.8412	22.5	0.8344	23.2	0.8189
Louis Botha/ Durban	0240808A/0240808A2	24.6	0.7896	25.3	0.7757	26.2	0.7586
Bloemfontein JBM Hertzog	2615161	25.1	0.7796	25.2	0.7777	25.9	0.7642
Kimberly	0290468A9	26.1	0.7605	26.8	0.7476	27.4	0.7369
Uppington	3174741	28.9	0.7114	29.7	0.6986	29.6	0.7002
Bethlehem	3315859	21.2	0.8647	22.9	0.8254	22.6	0.8321
Pretoria	0513314AX/C9	25.1	0.7796	26.7	0.7494	26.4	0.7549
Nelspruit-Friedenheim	5558665	23.3	0.8167	23.1	0.8211	26.9	0.7458
Pietersburg	0677802A5/0677802BX	25.2	0.7777	26	0.7623	25	0.7816

[redacted]

Average, Copt(1995-1999) [redacted]

APPENDIX D: **INFORMATION ON THE SIMPLIFIED GEOLOGY OF SOUTH AFRICA AND FLUORINE CONTAINING ROCKS**

Table 29: Fluorine in intrusive and extrusive igneous rocks. 'Tr' is trace, All concentrations in mg/kg

Rock Type	Rang e		Mean	Number
	Min	Max		
Intrusive				
Ultramafic	Tr.	2000	130	37
Gabbros	50	11000	430	47
Diorites	300	1300	665	20
Granites and Granodiorites	20	30 000	810	182
Syenite and monzonite	200	4 000	1 360	26
Alkaline ultramafic	Tr.	3 800	1 400	41
Alkali syenite	100	25 800	1 800	249
Alkali granite	670	12 400	5 500	20
Carbonatites	200	24 000	8 100	96
Kimberlites	520	2 500	1 310	42
Dolerites	198	500	420	14
Pegmatites	800	9 000	4 320	6
Extrusive				
Basalts	20	2 400	375	317
Andesites	Tr.	1 200	250	97
Rhyolites	Tr.	6 850	610	151
Trachyte and Latite	200	2 250	750	9

Table 30: Fluorine in metamorphic rocks. Concentrations in mg/kg, WRC, 2001.

Rock Type	Range		Mean	Number
	Min	Max		
		Regional		
Metagabbro	99	140	120	2
Schists	60	580	250	48
Amphibolite	140	1 400	740	10
Gneiss	240	2 800	1030	14
	Metasomatic			
Hornfels	26	7 800	1 630	57
Contact Skarns	700	43 500	9 780	28
Greisens	1 600	20 400	9 800	26
Kaolinized Granite	800	7 400	2 800	26
Fenite	Tr.	600	400	3

Table 31: Fluorine in sedimentary rocks. Concentrations in mg/kg, WRC, 2001

Rock Type	**Range**		**Mean**	**Number**
	Min	**Max**		
		Clastic		
Shales, siltstones and mudstones	10	11 660	790	141
Sandstones and Greywackes	10	880	180	49
Oceanic sediments	100	1 600	640	151
		Biogenic /	Chemical	
Limestone	Tr.	1 210	220	98
Dolomite	110	400	260	14
Phosphate Rock	10 400	42 000	30 500	74
Anhydrite and Gypsum	130	890	600	6
Rock salt	2	6	5	4

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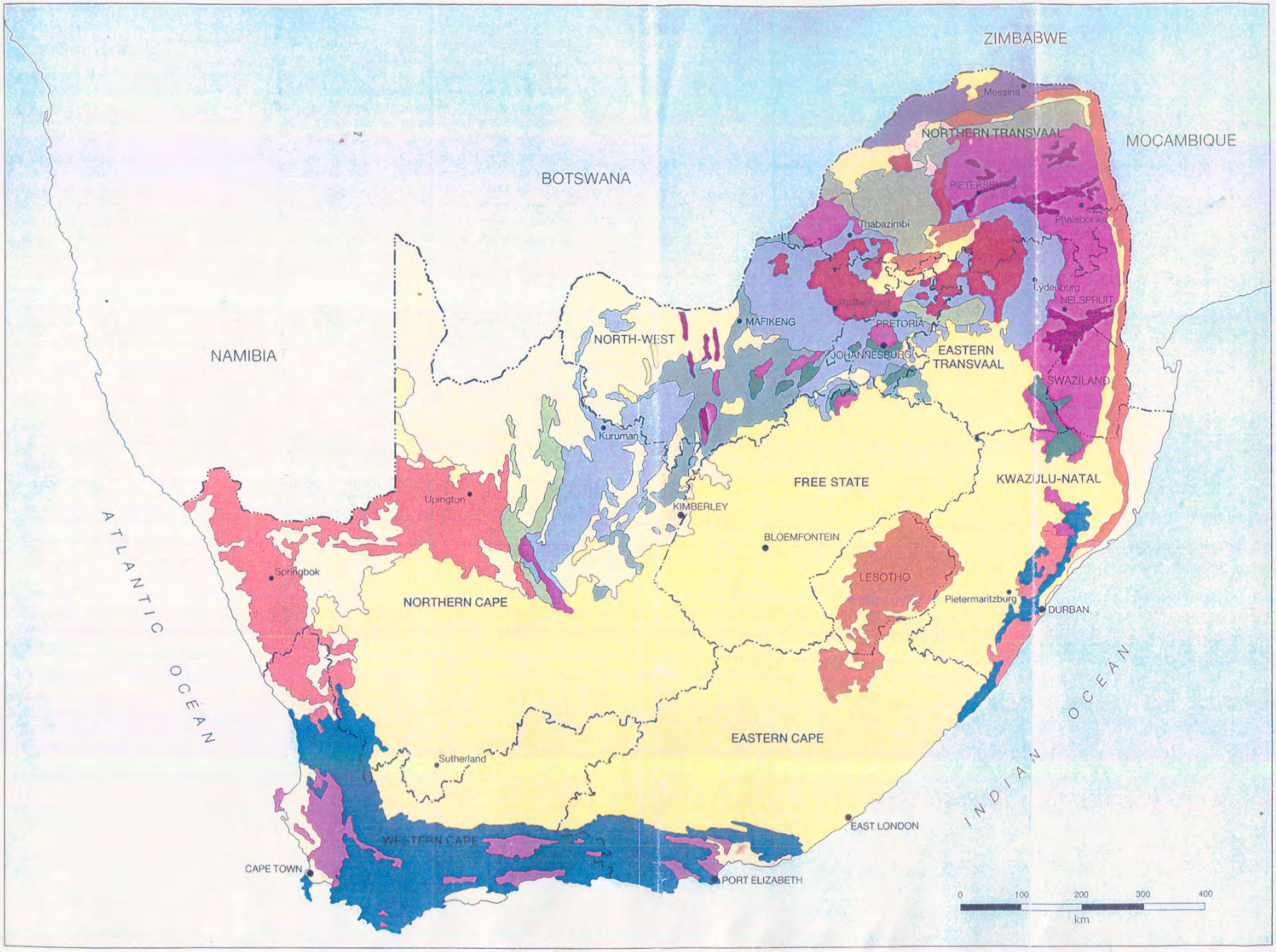
Simplified Geology of the Republic of South Africa

(Including Lesotho and Swaziland)

The geological formations illustrated on this map range from some of the oldest known on Earth, for exampl the Barberton Supergroup, to modern-day deposits and sand dunes of the Kalahari. Many rock-types are fou in these geological formations. Sedimentary conglomerates, sandstones and shale form large sections of tl Witwatersrand, Cape and Karoo Supergroups; limestones, dolomites and iron-formations occur in the Transva Supergroup; metamorphic granulites, amphibolites and schists outcrop in the Limpopo region, the Northe Cape Province and Namaqualand; igneous granites constitute parts of the Kaapvaal Craton in the Northern ai Eastern Transvaal Provinces; gabbros and other chrome-rich and platinum-rich igneous rocks are found in tl Bushveld Complex, and ancient volcanic lavas form the Ventersdorp Supergroup and the uppermost portion the Karoo Supergroup. Adapted from the 1:4 million (1986) "Geological Map of Southern Africa", Geologic Society of South Africa.

ROCK TYPES	STRATIGRAPHY	AGE (million years)	MAIN MINERALS
Recent cover (sand, alluvium)	Quaternary, Tertiary	0-65	Diamonds
Lava (basalt, rhyolite)	Karoo Supergroup	150-300	Amethyst, agates, zeolites
Sediments (sandstone, shale, siltstone) and dolerite			Fluorite, prehnite, barite platinoids, gypsum
Sediments (sandstone, quartzite, shale)	Cape Supergroup	320-500	Manganese, gold, tin
Granite, sediments (limestone)	Cape granites, Malmesbury	500-600	Tin, aragonite (caves)
Meta-sediments, meta-volcanics (gneisses, pegmatites, etc.)	Namaqua-Natal Region	600-1 500	Beryl, tantalite, corundum, lead-zinc copper, quartz
Sediments (arkoses, conglomerate)	Waterberg Group	1 750-1 850	
Igneous intrusions, etc. (gabbro, "Red" granite, anorthosite)	Bushveld, Phalaborwa Complexes	1 900-2 100	Tin, platinum, chromite, lead-zinc, andalusite, garnet, magnesite, zeoli
Sediments (dolomite, limestone, iron-formations, shale, quartzite)	Transvaal Supergroup	2 200-2 500	Manganese, lead-zinc, iron, asbestos, "Tigers eye", jasper
Lavas (basalt, andesite, porphyry)	Ventersdorp Group	2 500-2 700	Agates
Metamorphics (gneisses, granulites, schist)	Limpopo Province	±2 700-3 500	Copper, garnet, corundum, nickel
Sediments, volcanics (quartzites, conglomerate, lava)	Witwatersrand, Pongola Supergroups	2 700-3 100	Gold, quartz, jasper
Granites, tonalites, granitoids	Ancient granitic crust	3 000-3 100	Tin, tantalite, corundum beryl, emeralds
Sediments, volcanics (sandstones, conglomerate, komatiites, pyroxenites)	"Greenstones": Barberton, Murchison, Pietersburg	3 000-3 500	Gold, nickel, mercury, antimony, copper-zinc, asbestos


ZIMBABWE
Messina
NORTHERN TRANSVAAL
MOÇAMBIQUE
BOTSWANA
Thabazimbi
Phalaborwa
Lydenburg
NELSPRUIT
MAFIKENG
PRETORIA
NORTH-WEST
NAMIBIA
JOHANNESBURG
EASTERN
TRANSVAAL
SWAZILAND
Kuruman
FREE STATE
KWAZULU-NATAL
Upington
KIMBERLEY
ATLANTIC OCEAN
BLOEMFONTEIN
Springbok
LESOTHO
NORTHERN CAPE
Pietermaritzburg
DURBAN
Sutherland
EASTERN CAPE
INDIAN OCEAN
WESTERN CAPE
EAST LONDON
CAPE TOWN
PORT ELIZABETH
0
100
200
300
400
km